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AMERICAN

CHEMICAL JOURNAL

THE OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS AT 10°.[1]

By H. N. Morse and W. W. Holland.

The present measurements of the osmotic pressure of glucose solutions have been made under much more satisfactory conditions than those of any previous series. It is recalled here that the earlier work was beset with certain well-defined difficulties which it was necessary to overcome before any high degree of precision could be ascribed to the results. The first of these difficulties was the phenomenon to which the name *"thermometer effects"* was given.[2] When the temperature of a solution in a closed cell rises, the solution expands more rapidly and to a greater extent than the containing vessel; and, unless the change of temperature is exceedingly slow—so slow, in fact, that the expulsion of water from the solution through the membrane can keep pace with the expansion of the cell contents, there is an abnormally high pressure created which may considerably exceed the true osmotic pressure. On the other hand,

[2] *Ibid.*, **34**, 23 and 92; **36**, 1.

when the temperature falls, the reverse occurs; the enclosed solution contracts more than the containing cell, and, if the water from without cannot enter with sufficient rapidity—as it usually cannot—an abnormally low pressure is observed. It has been found that in "slow" cells—*i. e.*, those whose membranes, owing to small area or great thickness, do not permit the rapid passage of water—the thermometer effects may even persist for several hours after the bath has recovered its normal temperature. It may be noted here that the effect of attempting to measure osmotic pressure by balancing against it mechanical pressure is, in one way, similar to the thermometer effects of rising bath temperatures. The pressure in the cell, owing to the slow escape of the solvent, rises, if the membrane is not ruptured, above the normal osmotic pressure. In another way, the two are dissimilar. The solution which has been subjected to an excessive mechanical pressure becomes permanently more concentrated than before, while the other recovers after a time its original concentration. The fluctuations after the cells had reached their maximum pressures which are to be observed in the published records of earlier determinations were frequently due to thermometer effects.

The necessity of maintaining a very nearly constant temperature throughout any given experiment became more and more apparent as the work progressed and much attention has therefore been given to devising the means by which this could be accomplished automatically and with certainty. The result has been the development of a somewhat complete system of temperature regulation for baths which will be described later, together with other important modifications of our method. For present purposes, it is sufficient to say that the results presented in this and in the preceding paper[1] are less affected by fluctuating bath temperatures than those of the earlier work.

A second source of error which gave much trouble in the earlier measurements of pressure was the upward displacements of the manometers and the distortion of the rubber stoppers,[2] both of which led to an increase of unknown amount in the

[1] This Journal, **39**, 667.
[2] *Ibid.*, **36**, 23 and 50; **37**, 327, 460 and 580; **38**, 178.

capacity of the cell, and a consequent dilution of the solutions. If this had been the only source of dilution, it would be of little importance; but, since there were others, and it was necessary, for the proper correction of the results, to discriminate between dilution which occurred before and after the measurement of pressure, the difficulty was a serious one, leaving, as it sometimes did, a considerable margin of uncertainty as to the precise concentration of the solution whose pressure had been determined. The displacement of the manometer and the distortion of the stopper, however, were brought under tolerably good control immediately after the first three series of measurements had been completed, and that control has been continuously perfected, until the present results may be declared entirely free from sensible error due to the causes in question.

The third difficulty, and the most obstinate one of all, was the dilution of the solutions which occurred while the cells were being closed and opened.[1] The perplexities which result from such a dilution have been much discussed in former papers, but without entirely satisfactory results. The portion of the dilution which occurs while the cell is being closed precedes the measurement of pressure, and the result should be corrected for it; but that which occurs while the cell is being opened is subsequent to the measurement, and therefore without effect on the pressure. Unfortunately we had no means of determining how the dilution of the cell contents was to be distributed between the two periods, though we expressed the conviction that *not less* than half of it occurred while the cell was being opened. There was, under the circumstances, but one thing to do, and that was to devise means of suppressing *all dilution* of the cell contents, and this has, at last, been very nearly accomplished, as will be seen by inspecting the tabulated data contained in this, and in the preceding paper.

One important result of the suppression of practically all dilution in the cell is the definite location of the principal period of dilution. The corrective measures were directed against that portion of it which occurs while the cell is being opened, and it was found, when this had been eliminated, that nearly

[1] This Journal, **36**, 26 and 49; **37**, 328, 427, 463, 559 and 582.

all loss in concentration had disappeared.   In 12 of the series of
19 measurements of pressure presented in this paper (see Table
XX.) there was no loss of concentration whatever, and in the re-
maining 7, the largest dilution observed amounted to a correc-
tion of only o.10 of an atmosphere in a total osmotic pressure
of 21.38 atmospheres.   The record was equally satisfactory in
the paper[1] which preceded this, in which an account is given of
20 measurements of the osmotic pressure of cane sugar solutions
at 10°.   In 12 of these, there was no ascertainable loss of rota-
tion, and in the remaining 8, the largest correction for such loss
was only o.09 atmosphere in a total osmotic pressure of 24.97
atmospheres.   A part of even this loss is undoubtedly to be
ascribed to inversion, since it has been shown in an earlier paper
that a slight inversion of cane sugar always occurs in the osmotic
cell.

Very substantial progress has also been made during the past
year in the methods of calibrating, comparing, and testing the
manometers, all of which has contributed materially to the
exactness of the more recent results.   The manometers are now
filled with nitrogen instead of air, it having been found[2] that,
however carefully purified the mercury may be, there is always
a slow diminution of the volumes of air in a manometer.   This
apparent decrease of volume could be accounted for by suppos-
ing the tubes to stretch under pressure, and the question
whether they do sensibly expand under the pressures to which
we subject them is being investigated.

We are now prepared to give a conditional answer to a ques-
tion which is often asked; namely, how closely, in our judgment,
are we able to measure osmotic pressure?   Unless there are
constant sources of error of which we are unaware, and unless
the remaining known sources of error are greater than we be-
lieve them to be, the uncertainties of our present measurements
are confined to the second decimal place of the figures expressing
the osmotic pressures.   This opinion cannot be justified with-
out an elaborate discussion of all the essential details of our
method in its present and much altered form, but one bit of

[1] THIS JOURNAL, **39**, 667.
[2] *Ibid.*, **37**, 326.

evidence of considerable value can be secured from the data contained in the present paper. It will be seen from Table XX., which gives a summary of the results, that the duplicate determinations of eight concentrations differed by only 0.01 atmosphere, while in two other cases, they differed by 0.04 atmosphere. The differences between duplicate determinations were also confined to the second decimal place throughout the series of measurements[1] of the pressure of cane sugar solutions at 10°. The possibilities of improvement are, however, not exhausted with the removal of the larger sources of error mentioned above, *i. e.*, displacement of the manometer and distortion of the stopper, thermometer effects, and dilution of the solution within the cell. There remain several minor sources of error, some well known and others suspected, which will hereafter receive attention in the order of their supposed relative importance.

Table I.

0.1 Wt. normal solution. Ex. No. 1. *Rotation:* (1) original, 5°.15; (2) at conclusion of expr., 5°.1; loss, 0.05 = 0.96 per cent. *Manometer:* No. 8; volume of nitrogen, 473.20; displacement, 0.08 mm. Cell used, B. Resistance of membrane, 187,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.47; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.06. Time of setting up cell, 4.00 P.M., Jan. 11, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 14.						
3.00 P.M.	10°.1	11°.1	163.80	2.38	2.31	0.07
11.00 "	10°.1	10°.9	163.35	2.38	2.31	0.07
Jan. 15.						
9.00 A.M.	10°.1	10°.8	162.70	2.39	2.31	0.08
				2.38	2.31	0.07

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.036.

[1] This Journal, **39**, 667.

Table II.

o.1 Wt. normal solution.   Exp. No. 2.   *Rotation:* (1) original, 5°.1; (2) at conclusion of expr., 5°.1; loss, o.   *Manometer:* No. 9; volume of nitrogen, 432.90; displacement, o.05 mm.   Cell used, B.   Resistance of membrane, 280,-000.   *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, o.44; (3) dilution, o; (4) concentration, o; (5) capillary depression, o.02.   Initial pressure, 2.13.   Time of setting up cell, 12.00 M., Jan. 18, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Jan. 20.						
12.00 M.	10°.2	10°.4	146.58	2.37	2.31	0.06
Jan. 21.						
10.00 A.M.	10°.2	10°.8	145.52	2.40	2.31	0.09
1.00 P.M.	10°.2	11°.0	145.40	2.40	2.31	0.09
				2.39	2.31	0.08

Molecular osmotic pressure, 23.90.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.034.

Table III.

o.2 Wt. normal solution.   Exp. No. 1.   *Rotation:* (1) original, 10°.5; (2) at conclusion of expr., 10°.5; loss, o.   *Manometer:* No. 8; volume of nitrogen, 473.20; displacement, o. Cell used, H.   Resistance of membrane, 180,000.   *Corrections:* (1) atmospheric pressure, o.98; (2) liquids in manometer, o.55; (3) dilution, o; (4) concentration, o; (5) capillary depression, o.02.   Initial pressure, 3.2.   Time of setting up cell, 3.00 P.M., Jan. 24, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Jan. 27.						
9.00 A.M.	10.°4	10°.6	91.13	4.78	4.63	0.15

Note—Only one satisfactory reading was obtained in this experiment.

Molecular osmotic pressure, 23.90.
Molecular gas pressure, 23.15.
Ratio of osmotic to gas pressure, 1.032.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 10°.5; (2) at conclusion of expr., 10°.5; loss, o. *Manometer:* No. 9; volume of nitrogen, 432.90; displacement, o. Cell used, B. Resistance of membrane, 220,000. *Corrections:* atmospheric pressure, 0.98; (2) liquids in manometer, 0.51; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 3.6. Time of setting up cell, 4.00 P.M., Jan. 24, 1908.

	Temperature.		Volume	Pressure.		
Time. Jan. 27.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference
11.00 A.M.	10°.2	10°.4	83.47	4.74	4.61	0.13

Note—As in the first experiment with the 0.2 normal solution, only one satisfactory reading was obtained.

Molecular osmotic pressure, 23.70.
Molecular gas pressure, 23.05.
Ratio of osmotic to gas pressure, 1.028.

Table V.

0.3 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 15°.75; (2) at conclusion of expr., 15.°75; loss, o. *Manometer:* No. 8; volume of nitrogen, 473.2; displacement, 0.02 mm. Cell used, B. Resistance of membrane, 229,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.65; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 4.62. Time of setting up cell, 5.00 P.M., Jan. 29, 1908.

	Temperature.		Volume	Pressure.		
Time. Jan. 31.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
9.00 A.M.	10°.0	10°.6	63.61	7.10	6.92	0.18
12.00 M.	10°.0	10°.4	63.36	7.13	6.92	0.21
3.00 P.M.	10°.0	10°.6	63.66	7.09	6.92	0.17
				7.11	6.92	0.19

Note—The duplicate of this experiment was lost.

Molecular osmotic pressure, 23.70.
Molecular gas pressure, 23.07.
Ratio of osmotic to gas pressure, 1.027.

Table VI.

0.4 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 20°.8; (2) at conclusion of expr., 20°.8; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0. Cell used, H. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.14. Time of setting up cell, 4.00 P.M., Feb. 3, 1908.

Time. Feb. 5.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	10°.2	10°.6	41.97	9.51	9.24	0.27
11.30 "	10°.1	10°.6	42.00	9.49	9.24	0.25
2.00 P.M.	10°.1	10°.7	42.00	9.50	9.24	0.26
				9.50	9.24	0.26

Molecular osmotic pressure, 23.75.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.028.

Table VII.

0.4 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 20°.8; (2) at conclusion of expr., 20°.8; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0.09 mm. Cell used, H. Resistance of membrane, 185,000. *Corrections:* (1) atmospheric pressure, 1.02; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 6.4. Time of setting up cell, 4.00 P.M., Feb. 7, 1908.

Time. Feb. 8.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference
11.00 P.M.	10°.1	10°.3	41.72	9.55	9.24	0.31
Feb. 9.						
10.00 A.M.	10°.2	10°.3	41.78	9.53	9.24	0.29
				9.54	9.24	0.30

Molecular osmotic pressure, 23.85.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.032.

Table VIII.

o.5 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 25°.80; (2) at conclusion of expr., 25°.80; loss, o. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, o. Cell used, H. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 1.02; (2) liquids in manometer, o.58; (3) dilution, o; (4) concentration, o; (5) capillary depression, o.02. Initial pressure, 8.82. Time of setting up cell, 4.00 P.M., Feb. 11, 1908.

Time.	Temperature.		Volume	Pressure.		
Feb. 12.	Solution.	Manometer.	N$_2$.	Osmotic.	Gas.	Difference.
8.00 P.M.	10°.3	11°.6	33.80	11.92	11.56	0.36
Feb. 13.						
9.00 A.M.	10°.2	10°.6	33.80	11.92	11.55	0.37
12.00 M.	10°.05	10°.7	33.86	11.90	11.55	0.35
				11.91	11.55	0.36

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.11.
Ratio of osmotic to gas pressure, 1.031.

Table IX.

o.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 25°.8; (2) at conclusion of expr., 25°.8; loss, o. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, o.11 mm. Cell used, H. Resistance of membrane, 123,000. *Corrections:* (1) atmospheric pressure, o.98; (2) liquids in manometer, o.58; (3) dilution, o; (4) concentration, o; (5) capillary depression, o.02. Initial pressure, 9.11. Time of setting up cell, 4.00 P.M., Feb. 14, 1908.

Time.	Temperature.		Volume	Pressure.		
Feb. 15.	Solution.	Manometer.	N$_2$.	Osmotic.	Gas.	Difference.
8.00 P.M.	10°.2	11°.3	33.90	11.92	11.55	0.37
11.30 "	10°.0	10°.6	33.94	11.89	11.54	0.35
Feb. 16.						
10.00 A.M.	10°.0	10°.4	34.00	11.88	11.54	0.34
				11.90	11.54	0.36

Molecular osmotic pressure, 23.80.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.031.

Table X.

0.6 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 30°.8; (2) at conclusion of expr., 30°.8; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0.06 mm. Cell used, H. Resistance of membrane, 140,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.26. Time of setting up cell, 4.00 P.M., Feb. 17, 1908.

	Temperature.		Volume	Pressure.		
Time. Feb. 19.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
9.00 A.M.	10°.1	10°.6	28.41	14.29	13.85	0.44
12.00 M	10°.0	11°.0	28.40	14.29	13.84	0.45
3.00 P.M.	10°.2	10°.6	28.39	14.31	13.86	0.45
				14.30	13.85	0.45

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.032.

Table XI.

0.6 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 31°.65; (2) at conclusion of expr., 31°.65; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0.27 mm. Cell used, G. Resistance of membrane, 367,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.00. Time of setting up cell, 4.00 P.M., Mar. 20, 1908.

	Temperature.		Volume	Pressure.		
Time. Mar. 21.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
12.00 M.	10°.0	10°.6	28.35	14.29	13.84	0.45
6.00 P.M.	10°.0	10°.9	28.31	14.31	13.84	0.47
Mar. 22.						
10.00 A.M.	10°.0	10°.3	28.28	14.32	13.84	0.48
				14.31	13.84	0.47

Molecular osmotic pressure, 23.85.
Molecular gas pressure, 23.07.
Ratio of osmotic to gas pressure, 1.034.

Table XII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 35°.5; (2) at conclusion of expr., 35°.3; loss, 0°.2 = 0.56 per cent. *Manometer:* No. 11; volume of nitrogen, 407.37; displacement, 0.65 mm. Cell used, D. Resistance of membrane, 140,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.54; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.2. Time of setting up cell, 3.00 P.M., Mar. 2, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
Mar. 4.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 A.M.	10°.0	10°.7	23.91	16.68	16.16	0.52
Mar. 5.						
10.00 A.M.	10°.0	10°.3	23.91	16.68	16.16	0.52
5.00 P.M.	10°.1	11°.0	23.84	16.73	16.16	0.57
				16.70	16.16	0.54

Molecular osmotic pressure, 23.86.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.033.

Table XIII.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 35°.45; (2) at conclusion of expr., 35°.45; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0.14 mm. Cell used, G. Resistance of membrane, 500,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.43. Time of setting up cell, 6.00 P.M., Mar. 23, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
Mar. 24.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	10°.1	10°.7	24.43	16.67	16.16	0.51
Mar. 25.						
9.00 A.M.	10°.0	10°.6	24.41	16.67	16.16	0.51
12.00 M.	10°.0	10°.8	24.38	16.70	16.16	0.54
4.00 P.M.	10°.0	10°.7	24.38	16.70	16.16	0.54
				16.69	16.16	0.53

Molecular osmotic pressure, 23.84.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.033.

Table XIV.

0.8 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 40°.2; (2) at conclusion of expr., 40°.1; loss, 0.1=0.25 per cent. *Manometer:* No. 11; volume of nitrogen, 407.37; displacement, 0.30 mm. Cell used, D. Resistance of membrane, 367,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.55; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 16.00. Time of setting up cell, 4.00 P.M., Mar. 20, 1908.

Time. Mar. 21.	Temperature.		Volume N$_2$.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
1.00 P.M.	10°.0	10°.6	21.00	19.01	18.46	0.55
6.00 P.M.	10°.0	10°.9	20.96	19.04	18.46	0.58
11.00 P.M.	10°.15	10°.9	20.85	19.07	18.47	0.60
Mar. 22.						
10.00 A.M.	10°.0	10°.3	20.96	19.04	18.46	0.58
				19.04	18.46	0.58

Molecular osmotic pressure, 23.80.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.031.

Table XV.

0.8 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 40°.1; (2) at conclusion of expr., 40°.1; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0.04 mm. Cell used D. Resistance of membrane, 190,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.14. Time of setting up cell, 1.00 P.M., Mar. 29, 1908.

Time. Mar. 30.	Temperature.		Volume N$_2$.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
4.00 P.M.	10°.0	11°.8	21.42	19.06	18.46	0.60
8.00 P.M.	10°.0	11°.7	21.44	19.05	18.46	0.59
12.00 P.M.	10°.0	11°.4	21.43	19.05	18.46	0.59
				19.05	18.46	0.59

Molecular osmotic pressure, 23.81.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.032.

Table XVI.

0.9 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 44°.70; (2) at conclusion of expr., 44°.55; loss, 0°.15= 0.34 per cent. *Manometer:* No. 14; volume of nitrogen, 420.6; displacement, 0.22 mm. Cell used, D. Resistance of membrane, 150,000. *Corrections:* (1) atmospheric pressure, 1.02; (2) liquids in manometer, 0.59; (3) dilution, 0.07; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 13.66. Time of setting up cell, 11.30 A.M., Mar. 8, 1908.

Time. Mar. 10.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	10°.0	10°.3	19.35	21.39	20.77	0.62
12.30 P.M.	10°.1	10°.4	19.36	21.37	20.78	0.59
Mar. 11.						
8.00 A.M.	10°.2	10°.2	19.37	21.42	20.79	0.63
				21.39	20.78	0.61

Molecular osmotic pressure, 23.77.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.030.

Table XVII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 44°.80; (2) at conclusion of expr., 44°.60; loss, 0°.20 = 0.45 per cent. *Manometer:* No. 14; volume of nitrogen, 420.6; displacement, 0.42 mm. Cell used, D. Resistance of membrane, 275,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.59; (3) dilution, 0.10; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 15.87. Time of setting up cell, 4.00 P.M., Mar. 26, 1908.

Time. Mar. 27.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
5.00 P.M.	10°.0	11°.1	19.41	21.38	20.77	0.61
11.00 P.M.	10°.0	10°.8	19.42	21.38	20.77	0.61
Mar. 28.						
9.00 A.M.	10°.0	10°.9	19.41	21.38	20.77	0.61
				21.38	20.77	0.61

Molecular osmotic pressure, 23.76.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.029.

Table XVIII.

1.0 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 49°.15; (2) at conclusion of expr., 49°.00; loss, 0°.15= 0.3 per cent. *Manometer:* No. 14; volume of nitrogen, 420.6; displacement, 0.17 mm. Cell used, D. Resistance of membrane, 124,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0.07; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.05. Time of setting up cell, 4.00 P.M., Mar. 16, 1908.

Time. Mar. 17.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
5.00 P.M.	10°.1	11°.1	17.46	23.80	23.09	0.71
Mar. 18.						
4.00 P.M.	10°.0	10°.9	17.47	23.77	23.08	0.69
10.00 P.M.	10°.0	10°.9	17.46	23.79	23.08	0.71
Mar. 19.						
9.00 A.M.	10°.0	10°.7	17.46	23.78	23.08	0.70
				23.79	23.08	0.71

Molecular osmotic pressure, 23.79.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.031.

Table XIX.

1.0 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 49°.35; (2) at conclusion of expr., 49°.15; loss, 0°.2= 0.41 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.61 mm. Cell used, D. Resistance of membrane, 500,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.62; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.00. Time of setting up cell, 5.00 P.M., Mar. 23, 1908.

Time. Mar. 24.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	10°.1	10°.7	16.85	23.79	23.09	0.70
Mar. 25.						
9.00 A.M.	10°.0	10°.6	16.84	23.79	23.08	0.71
12.00 M.	10°.0	10°.8	16.83	23.81	23.08	0.73
4.00 P.M.	10°.0	10°.7	16.84	23.80	23.08	0.72
				23.80	23.08	0.72

Molecular osmotic pressure, 23.80.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.031.

Table XX.—*Summary of Results.*

Concentration.	Temperature.	Loss in rotation.	Correction for dilution.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	10°.10	0°.05	0.02	2.38	2.31	0.07	23.83	23.09	1.036
0.1	10°.20	0°.00	0.00	2.39	2.31	0.08	23.90	23.10	1.034
0.2	10°.40	0°.00	0.00	4.78	4.63	0.15	23.90	23.15	1.032
0.2	10°.20	0°.00	0.00	4.74	4.61	0.13	23.70	23.05	1.028
0.3	10°.00	0°.00	0.00	7.11	6.92	0.19	23.70	23.07	1.027
0.4	10°.10	0°.00	0.00	9.50	9.24	0.26	23.75	23.10	1.028
0.4	10°.10	0°.00	0.00	9.54	9.24	0.30	23.85	23.10	1.032
0.5	10°.20	0°.00	0.00	9.91	11.55	0.36	23.83	23.11	1.031
0.5	10°.15	0°.00	0.00	11.90	11.54	0.36	23.80	23.10	1.032
0.6	10°.10	0°.00	0.00	14.30	13.85	0.45	23.83	23.08	1.031
0.6	10°.10	0°.00	0.00	14.31	13.84	0.47	23.85	23.07	1.034
0.7	10°.20	0°.00	0.00	16.70	16.16	0.54	23.86	23.09	1.033
0.7	10°.10	0°.20	0.09	16.69	16.16	0.53	23.84	23.09	1.033
0.8	10°.05	0°.00	0.00	19.04	18.46	0.58	23.80	23.08	1.031
0.8	10°.00	0°.10	0.05	19.05	18.46	0.59	23.81	23.08	1.032
0.9	10°.10	0°.00	0.00	21.39	20.78	0.61	23.71	23.09	1.030
0.9	10°.00	0°.15	0.07	21.38	20.77	0.61	23.76	23.08	1.029
1.0	10°.00	0°.15	0.10	23.79	23.08	0.71	23.79	23.08	1.031
1.0	10°.00	0°.20	0.07	23.80	23.08	0.72	23.80	23.08	1.031

Table XXI.—Summary of Results—Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for dilution.	Osmotic pressure.	Gas pressure.	Difference.
0.1	$10°.15$	$0°.03$	0.01	2.39	2.31	0.08
0.2	$10°.30$	$0°.00$	0.00	4.76	4.62	0.14
0.3	$10°.00$	$0°.00$	0.00	7.11	6.92	0.19
0.4	$10°.10$	$0°.00$	0.00	9.52	9.24	0.28
0.5	$10°.15$	$0°.00$	0.00	11.91	11.55	0.36
0.6	$10°.05$	$0°.00$	0.00	14.31	13.85	0.46
0.7	$10°.00$	$0°.10$	0.05	16.70	16.16	0.54
0.8	$10°.00$	$0°.05$	0.03	19.05	18.46	0.59
0.9	$10°.05$	$0°.18$	0.09	21.39	20.78	0.61
1.0	$10°.00$	$0°.18$	0.09	23.80	23.08	0.72

Concentration.	Temperature.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	$10°.15$	23.87	23.10	1.035
0.2	$10°.30$	23.80	23.10	1.030
0.3	$10°.00$	23.70	23.07	1.027
0.4	$10°.10$	23.80	23.10	1.030
0.5	$10°.15$	23.82	23.10	1.031
0.6	$10°.05$	23.84	23.08	1.033
0.7	$10°.00$	23.85	23.09	1.033
0.8	$10°.00$	23.81	23.08	1.032
0.9	$10°.05$	23.74	23.09	1.030
1.0	$10°.00$	23.80	23.08	1.031
		23.80	23.09	1.031

The conclusions to be drawn from the data contained in Tables I. to XIX., and summarized in Tables XX. and XXI., are:

1. That at 10° the osmotic pressure of glucose solutions is proportional to the concentration. This is best illustrated by means of the molecular pressures. The mean molecular pressure of the whole ten concentrations (see Table XXI.) is 23.80 atmospheres, while the highest and the lowest molecular pressures for the individual concentrations are 23.87 and 23.70 atmospheres, respectively. In respect to the proportionality of pressure to concentration, glucose behaves at 10° precisely as it was found to conduct itself at 0° and in the vicinity of 20°. It will be recalled that the freezing point depressions of glucose

solutions are also strictly proportional to their weight-normal concentration.

2. That the excess of osmotic over gas pressure which was observed in the neighborhood of 0° has not disappeared at 10°. The mean molecular osmotic pressure at the temperature employed in this series of measurements is 23.80 atmospheres, while the mean molecu'ar gas pressure is 23.09. The comparison is best made by means of the ratios given in the last column of Table XXI. It will there be seen that the mean ratio of osmotic to gas pressure, for all concentrations between 0.1 and 1.0 weight-normal solutions, is, at 10°, 1.031, while the maximum and minimum ratios for the individual concentrations are respectively 1.035 and 1.027. At 10° the osmotic pressure of glucose solutions is about 3.0 per cent higher than the gas pressure. At 0° the excess of osmotic over gas pressure was found to be about 5.0 per cent.

3. That the closer approximation of osmotic to gas pressure at 10° than at 0° is due in greater measure to the increase in gas pressure between these temperatures than to the augmentation of osmotic pressure. The mean molecular gas pressure at the temperatures around 0°, at which the former measurements were made, was 22.28 atmospheres, while for the present series of measurements around 10°, it is 23.09—an increase of 0.81 atmosphere. The mean molecular osmotic pressure at the lower temperature was found to be 23.45 atmospheres. At 10°, as noted above, it is 23.80—an increase of only 0.35 atmosphere. From evidence in hand we are inclined to believe that when we repeat the work at 0° under the better conditions which now prevail, we shall find a molecular osmotic pressure of about 23.36 atmospheres. If so, the increase between 0° and 10° will be 0.46 instead of 0.35 atmosphere. It appears that the increase in the osmotic pressure of glucose solutions from 0° to 10° is only about half as fast as the increase in gas pressure between those temperatures.

The first series of measurements of the osmotic pressure of glucose solutions was made at temperatures between 21°.7 and 26°.9. The mean ratio of osmotic to gas pressure at these temperatures was found to be 0.993, while the mean of the molecu-

lar osmotic pressures was 24.01 atmospheres, the mean molecular gas pressure being 24.19 atmospheres. The first series of measurements was, however, made under disadvantageous conditions. The means of regulating temperature were much less satisfactory than at present, the displacements of the manometers had not at that time been brought under good control, and dilution of the cell contents from other causes had not been suppressed. There was an average loss of rotation of 1.49 per cent, for all of which the results were corrected. We know now that some of this must have occurred while the cells were being opened and subsequent to the measurements of pressure. It is therefore probable that later work will modify for this series, by some fraction of 1.49 per cent, the osmotic gas ratio of 0.993, and, correspondingly, the mean molecular osmotic pressure of 24.01.

Below is given a tabular statement of the osmotic gas ratios and the mean molecular osmotic pressures thus far found for glucose solutions. Each series covers all the concentrations from 0.1 to 1.0 weight-normal.

	Temperatures.	Mean ratio of osmotic to gas pressure.	Mean molecular osmotic pressures.
Series I.	$21°.7–26°.9$	0.993	24.01 atmospheres.
" III.	$10°.0$	1.031	23.80 "
" II.	$0°.0$	1.052	23.45 "

The values for series III. will not, we think, be much modified by later investigation, but those of series I. and II. will probably be slightly altered, the former by some fraction of 1.49 per cent, and the latter by some fraction of 0.90 per cent—these numbers representing the average amount of the dilution which was observed in those series, regarding the proper correction for which some uncertainty still exists.

Johns Hopkins University,
    April 25, 1908.

CLVI. RESEARCHES ON PYRIMIDINES. THE ACTION OF NITRIC ACID ON 2,6-DIOXYPYRIMIDINES. OXYNITROHYDROTHYMINE.

[THIRTIETH PAPER.]

By Treat B. Johnson.

I shall describe, in this paper, some results which I have obtained by examining the behavior of fuming nitric acid towards 5-bromuracil, 5-chloruracil, and synthetical thymine.

In a paper entitled "Die Constitution des Thymins,"[1] Steudel has described the action of concentrated nitric acid on thymine. He obtained a compound to which he assigned the empirical formula $C_4H_4O_3N_4$. He gave no melting point for the compound, but states that it did not contain water of crystallization, that it was soluble in warm water and ammonia, and gave, on reduction, a derivative which responded to Weidel's alloxan reaction. I have repeated Steudel's experiment and have investigated the action of nitric acid of different concentrations and under various conditions, but in no case have I obtained a compound identical with his *nitrothymine*. The data which I have obtained seem to indicate that Steudel's *nitrothymine* was a secondary decomposition product, and not a simple thymine derivative.

Uracil, 5-bromuracil, 5-chloruracil, and thymine do not react, below 100°, with nitric acid of density 1.41. On the other hand, uracil dissolves, at ordinary temperature, in fuming nitric acid (sp. gr. 1.5), giving a good yield of 5-nitrouracil (I.). 5-Bromuracil, 5-chloruracil, and thymine react, under the same conditions, giving three derivatives corresponding to the empirical formulas II., III., and IV., respectively. The same compound IV. was also obtained when thymine was treated with concentrated nitric acid according to the directions of Steudel.[2]

Uracil, $\quad C_4H_4O_2N_2 \quad \longrightarrow C_4H_3O_2N_2(NO_2)$, I. (5-Nitrouracil).

5-Bromuracil, $C_4H_3O_2N_2(Br) \longrightarrow C_4H_3O_2N_2(Br)HNO_3$, II.

5-Chloruracil, $C_4H_3O_2N_2(Cl) \longrightarrow C_4H_3O_2N_2(Cl)HNO_3$, III.

Thymine, $\quad C_4H_3O_2N_2(CH_3) \longrightarrow C_4H_3O_2N_2(CH_3)HNO_3$, IV.
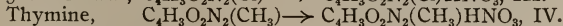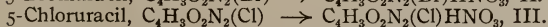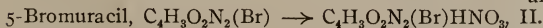
[1] Z. physiol. Chem., **32**, 241.
[2] *Loc. cit.*

I now find that the compound II., prepared from 5-bromuracil and nitric acid, is identical with *bromnitrooxyhydrouracil,* V., which Behrend[1] obtained by treatment of nitrouracil with bromine water. This interesting result, and the fact that the analogous compounds, III. and IV., are prepared under the same conditions, indicate that they have a similar structure and are to be considered as oxynitrohydropyrimidines; *viz.,* chlornitrooxyhydrouracil, VI., and oxynitrohydrothymine, VII., respectively:

$$
\begin{array}{ccc}
\mathrm{NH\!-\!\!-\!CO} & \mathrm{NH\!-\!\!-\!CO} & \mathrm{NH\!-\!\!-\!CO} \\
\mid \quad\;\; \mid \nearrow^{\mathrm{Br}} & \mid \quad\;\; \mid \nearrow^{\mathrm{Cl}} & \mid \quad\;\; \mid \nearrow^{\mathrm{CH_3}} \\
\mathrm{CO} \quad \mathrm{C} & \mathrm{CO} \quad \mathrm{C} & \mathrm{CO} \quad \mathrm{C} \\
\mid \quad\;\; \mid \searrow_{\mathrm{NO_2}} & \mid \quad\;\; \mid \searrow_{\mathrm{NO_2}} & \mid \quad\;\; \mid \searrow_{\mathrm{NO_2}} \\
\mathrm{NN\!-\!\!-\!CHOH} & \mathrm{NH\!-\!\!-\!CHOH} & \mathrm{NH\!-\!\!-\!CHOH} \\
\text{V.} & \text{VI.} & \text{VII.}
\end{array}
$$
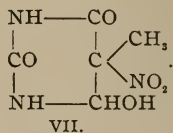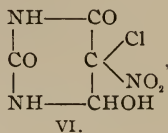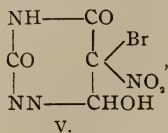
The formation of these hydropyrimidines involves a direct addition of nitric acid to the double bond between the 4 and 5 positions of the pyrimidine ring. The preparation of bromnitrooxyhydrouracil, V., from 5-nitrouracil and 5-bromuracil shows that the nitro group and bromine atom are linked to the same carbon atom. It also proves Behrend's[2] original conclusion that the formation of oxyhydropyrimidines, from certain pyrimidines, by the action of chlorine and bromine water involves an addition of hypochlorous and hypobromous acids at the double bond.

$$
\begin{array}{ccc}
\mathrm{NH\!-\!\!-\!CO} & \mathrm{NH\!-\!\!-\!CO} & \mathrm{NH\!-\!\!-\!CO} \\
\mid \quad\;\; \mid & \mid \quad\;\; \mid \nearrow^{\mathrm{Br}} & \mid \quad\;\; \mid \\
\mathrm{CO} \quad \mathrm{CBr} + \mathrm{HNO_3} \rightarrow & \mathrm{CO} \quad \mathrm{C} & \leftarrow \mathrm{H_2O} + \mathrm{Br_2} + \mathrm{CO} \quad \mathrm{CNO_2} \\
\mid \quad\;\; \parallel & \mid \quad\;\; \searrow_{\mathrm{NO_2}} & \mid \quad\;\; \parallel \\
\mathrm{NH\!-\!\!-\!CH} & \mathrm{NH\!-\!\!-\!CHOH} & \mathrm{NH\!-\!\!-\!CH} \\
& \text{V.} & \\
& \downarrow & \downarrow \\
\mathrm{NH\!-\!\!-\!CO} & & \mathrm{NH\!-\!\!-\!CO} \\
\mid \quad\;\; \mid \nearrow^{\mathrm{Br}} & & \mid \quad\;\; \mid \nearrow^{\mathrm{NO_2}} \\
\mathrm{CO} \quad \mathrm{C} & & \mathrm{CO} \quad \mathrm{C} \\
\mid \quad\;\; \mid \searrow_{\mathrm{OH}} & & \mid \quad\;\; \mid \searrow_{\mathrm{OH}} \\
\mathrm{NH\!-\!\!-\!CHNO_2} & & \mathrm{NH\!-\!\!-\!CHBr} \\
\text{VIII.} & & \text{IX.}
\end{array}
$$
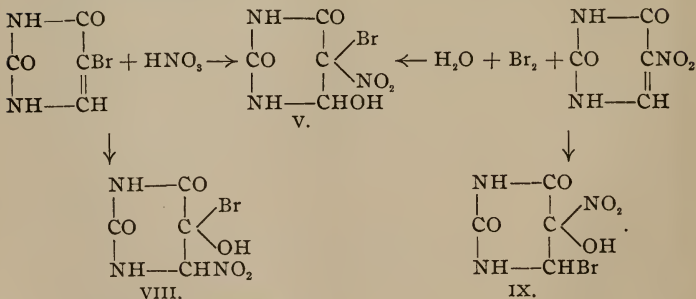
[1] Ann. Chem. (Liebig), **240**, 11.
[2] Ann. Chem. (Liebig), **229**, 20.

I also find that 5-bromuracil and 5-chloruracil react with chlorine water and bromine water, respectively, giving the same chlorbromoxyhydrouracil, X. When this hydropyrimidine was digested with alcohol it was converted into 5-chloruracil.

$$
\begin{array}{ccc}
\text{NH——CO} & \text{NH——CO} & \text{NH——CO} \\
|\quad\quad | & |\quad\quad |\,\diagup^{\text{Cl}} & |\quad\quad | \\
\text{CO}\quad \text{CBr} + H_2O + Cl_2 \rightarrow & \text{CO}\quad \text{C}\diagdown_{\text{Br}} \rightleftharpoons Br_2 + H_2O + & \text{CO}\quad \text{CCl} \\
|\quad\ \ \| & |\quad\quad | & |\quad\quad \| \\
\text{NH——CH} & \text{NH——CHOH} & \text{NH——CH} \\
& \text{X.} &
\end{array}
$$
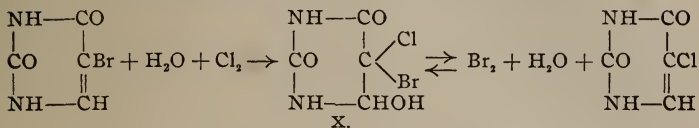
Thymine apparently shows no tendency to form salts with acids. It can be crystallized from concentrated hydriodic and hydrobromic acids without alteration. The possibility of the nitro derivative IV. being a nitric acid salt, XI. is excluded since thymine is not formed by treatment with alkalis, and also because it does not react with bromine water to give oxybromhydrothymine.[1] The compound is not a substituted nitro derivative, as represented by formulas XII., XIII., and XIV., because it does not contain water of crystallization. It can be crystallized repeatedly from absolute alcohol without alteration.

$$
\begin{array}{ccc}
\text{NH——CO} & \text{NO}_2\text{N——CO} & \text{NH——CO} \\
|\quad\quad | & |\quad\quad\quad | & |\quad\quad | \\
\text{CO}\quad \text{CCH}_3.\text{HNO}_3 & \text{CO}\quad \text{CCH}_3.H_2O & \text{CO}\quad \text{CCH}_3.H_2O \\
|\quad\quad \| & |\quad\quad\quad \| & |\quad\quad \| \\
\text{NH——CH} & \text{NH——CH} & \text{NO}_2\text{N——CH} \\
\text{XI.} & \text{XII.} & \text{XIII.}
\end{array}
$$

$$
\begin{array}{c}
\text{NH——CO} \\
|\quad\quad | \\
\text{CO}\quad \text{CCH}_2\text{NO}_2.H_2O. \\
|\quad\quad \| \\
\text{NH——CH} \\
\text{XIV.}
\end{array}
$$
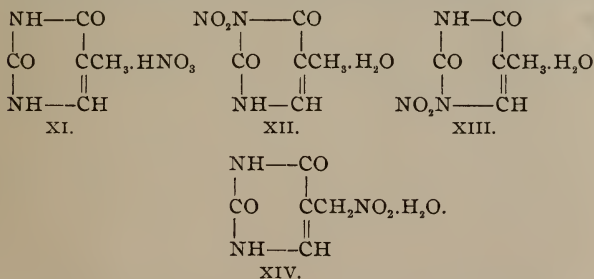
I have made the interesting observation that oxynitrohydrothymine, VII., can exist in two modifications which I have designated by the Greek letters α and β. The two isomers are obtained under practically the same conditions. The α derivative is the stable modification and melts at 183°–185°. The β derivative melts at 230°–235° and rearranges to the α form at

[1] Jones: Z. physiol. Chem., **29**, 20.

ordinary temperature. The two isomers are especially characterized by their crystalline habit and are converted quantitatively into thymine when reduced with tin and hydrochloric acid. This interesting case of isomerism is possibly similar in nature to that recently observed by Osten.[1] He found, for example, that methylisodialuric acid, XV., and its diethyl ether, XVI., occur in two isomeric modifications which undergo reversible transformations in the presence of acids and alkalis.

$$
\begin{array}{cc}
\text{NH} \!-\!\!-\! \text{CO} & \text{NH} \!-\!\!-\! \text{CO} \\
| \qquad | \quad \diagup \text{OH} & | \qquad | \quad \diagup \text{OC}_2\text{H}_5 \\
\text{CO} \quad \text{C} \diagdown & \text{CO} \quad \text{C} \diagdown \\
| \qquad | \quad \diagdown \text{OH} & | \qquad | \quad \diagdown \text{OC}_2\text{H}_5 \\
\text{NH} \!-\!\!-\! \text{COH} & \text{NH} \!-\!\!-\! \text{COH} \\
\quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{XV.} & \text{XVI.}
\end{array}
$$
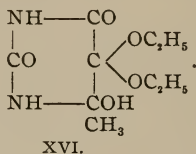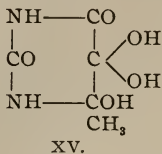
Oxynitrohydropyrimidines are probably formed in every case when 5-nitropyrimidines are obtained by the action of nitric acid. For example: the formation of nitrouracil from uracil probably involves an addition of nitric acid, giving the unstable hydropyrimidine XVII., which then breaks down with loss of a molecule of water, giving nitrouracil. In the case of thymine, on the other hand, the molecule cannot lose water in the normal manner and therefore the intermediate hydropyrimidine, VII., is capable of isolation.

$$
\begin{array}{l}
\text{NH}\!-\!\text{CO} \\
| \qquad | \\
\text{CO} \quad \text{CH} + \text{HNO}_3 = \\
| \qquad \| \\
\text{NH}\!-\!\text{CH}
\end{array}
\quad
\begin{array}{l}
\text{NH}\!-\!\text{CO} \\
| \qquad | \quad \diagup \text{NO}_2 \\
\text{CO} \quad \text{C} \diagdown \\
| \qquad | \quad \diagdown \text{H} \\
\text{NH}\!-\!\text{CHOH} \\
\qquad \text{XVII.}
\end{array}
\rightarrow
\begin{array}{l}
\text{NH}\!-\!\text{CO} \\
| \qquad | \\
\text{CO} \quad \text{CNO}_2 + \text{H}_2\text{O}. \\
| \qquad \| \\
\text{NH}\!-\!\text{CH}
\end{array}
$$
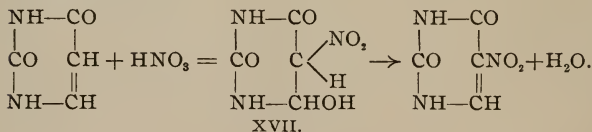
It is interesting to note here the behavior of nitric acid towards hydrouracil.[2] This compound contains no double bond between the 4 and 5 positions and the 5 position is not the point of attack. It reacts with nitric acid, giving a nitro derivative, XVIII., in which the nitro group is linked to the 3 position of the pyrimidine ring.

[1] Ann. Chem. (Liebig), **343**, 133.
[2] Franchimont and Friedmann: Rec. trav. chim., **26**, 218.

$$
\begin{array}{ccc}
\text{NH} \underline{\quad} \text{CO} & & \text{NH} \underline{\quad} \text{CO} \\
| \quad\quad | & & | \quad\quad | \\
\text{CO} \quad \text{CH}_2 + \text{HNO}_3 = & & \text{CO} \quad \text{CH}_2 + \text{H}_2\text{O}. \\
| \quad\quad | & & | \quad\quad | \\
\text{NH} \underline{\quad} \text{CH}_2 & & \text{NO}_2\text{N} \underline{\quad} \text{CH}_2
\end{array}
$$

<div align="center">XVIII.</div>
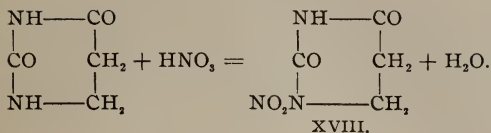
The isolation of the above oxynitrohydropyrimidines lends new interest to some early observations on the action of nitric acid on certain benzene derivatives. For example: nitric acid reacts with toluene, in presence of sulphuric acid, giving 3, 5-dinitroparacresol, XIX., and 3,5-dinitroorthocresol, XX.[1] Orthoxylene gives a mixture of 3,5-dinitroparaxylenol, XXI., and 3,5-dinitroorthoxylenol,[2] XXII. Orthocresolsulphonic acid reacts with nitric acid, giving 3,5-dinitroorthocresol,[3] XX. Similar observations have also been made in the naphthalene series.[4] Armstrong explains these abnormal reactions by assuming an addition of nitric acid to a double bond in the benzene ring, giving unstable addition products. These then break down in two ways, either with separation of nitrous acid, giving a phenol, or with loss of water, giving a nitro derivative.

XIX.   XX.   XXI.
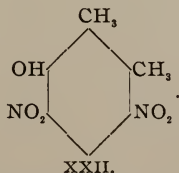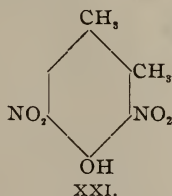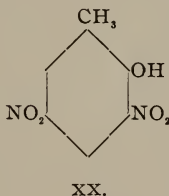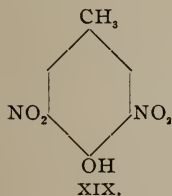
XXII.

[1] Nolting and Forel: Ber. d. chem. Ges., **18**, 2670.

[2] Nolting and Pick: *Ibid.*, **21**, 3158.

[3] Claus and Jackson: J. prakt. Chem. (2), **38**, 333.

[4] Armstong and Rossiter: P. Chem. Soc., **1891**, 87–89; Ber. d. chem. Ges., **24**, R. 721.

The action of nitric acid on orthocresolsulphonic acid, XXIII., may be represented by the following equation. The writer is not aware that such intermediate addition products with nitric acid have been isolated in the benzene series.

$$
\begin{array}{c}
\text{CH}_3 \\
\text{H} \underset{\text{H}}{\bigcirc} \overset{\text{OH}}{\underset{\text{SO}_3\text{H}}{}} \quad + 2\text{HNO}_3 = \quad
\text{H} \underset{\substack{\text{NO}_2 \\ \text{H}}}{\overset{\text{CH}_3}{\bigcirc}} \overset{\text{OH}}{\underset{\text{OH}}{\underset{\substack{\text{SO}_3\text{H} \\ \text{NO}_2}}{}}} \quad \rightarrow \\
\text{H} \\
\text{XXIII.}
\end{array}
$$

$$
\text{CH}_3 \\
\text{H} \underset{\substack{\text{NO}_2 \\ \text{H}}}{\overset{}{\bigcirc}} \overset{\text{OH}}{\underset{\text{NO}_2}{}} \quad + \text{H}_2\text{O} + \text{H}_2\text{SO}_4. \\
\text{XX.}
$$
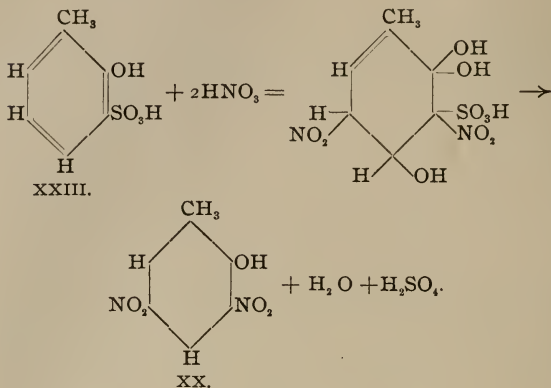
EXPERIMENTAL PART.

The Action of Nitric Acid (sp. gr. 1.5) on 5-Bromuracil.

Oxynitrobromhydrouracil,
$$
\begin{array}{c}
\text{NH}\!-\!\!-\!\text{CO} \\
|\qquad\quad | \;\diagup\text{Br} \\
\text{CO}\qquad \text{C}\!\!<\\
|\qquad\quad | \;\diagdown\text{NO}_2 \\
\text{NH}\!-\!\!-\!\text{CHOH}
\end{array}
$$
.—This compound
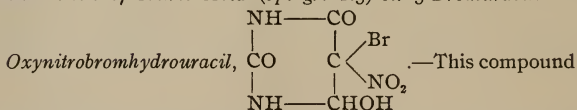
was first described by Behrend.[1] I prepared it in the following manner: Three grams of finely pulverized 5-bromuracil were dissolved in 19 cc. of nitric acid and the solution allowed to evaporate in a vacuum over sulphuric acid. I obtained 3.3 grams of the pure hydropyrimidine which crystallized in large blocks and rectangular prisms. The pyrimidine had no definite melting point, but decomposed from 150° to 165° according to the rate of heating. It was difficultly soluble in cold water but could not be purified by recrystallization from this solvent. When warmed with water above 40° it was decomposed with

[1] *Loc. cit.*

formation of brompicrin, which was recognized by its disagreeable odor. The pyrimidine did not contain water of crystallization. It agreed in its chemical behavior, so far as I was able to judge, with the hydropyrimidine described by Behrend.

0.3006 gram of substance gave 0.2204 gram CO_2 and 0.0481 gram H_2O. Nitrogen (Kjeldahl).

	Calculated for $C_4H_4O_5N_2Br$.	I.	Found. II.
C	19.00	20.00	. . .
H	1.57	1.77	. . .
N	16.53	. . .	16.35

Reduction of Oxynitrobromhydrouracil with Tin and Hydrochloric Acid.—Two grams of the hydropyrimidine were reduced, on the steam bath, for one hour with an excess of tin and hydrochloric acid. The solution was then evaporated to dryness to remove the excess of hydrochloric acid and the residue redissolved in water. The tin was then removed by precipitation with hydrogen sulphide and the filtrate concentrated to a volume of 20 cc. Five grams of potassium cyanate were then added to the solution when I obtained an insoluble, granular precipitate. The compound was difficultly soluble in hot water and practically insoluble in the common organic solvents and dilute sulphuric acid. It did not contain halogens, and left no inorganic residue when burned on a platinum foil. When the compound was warmed with bromine water and then treated with an excess of barium hydroxide solution, a purple precipitate was obtained. Its characteristic properties and nitrogen determinations identified the compound as Behrend's[1] *hy-*

$$\text{droxyxanthine,} \quad \begin{array}{c} NH\!-\!\!-\!\!CO \\ | \qquad | \\ CO \qquad CNHCONH_2. \\ | \qquad \| \\ NH\!-\!\!-\!\!CH \end{array}$$
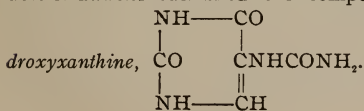
Nitrogen (Kjeldahl):

	Calculated for $C_5H_6O_5N_4$.	I.	Found. II.
N	32.94	32.80	32.95

[1] Ann. Chem. (Liebig), **229**, 40; **240**, 6.

Oxydichlorhydrouracil,
$$\begin{array}{c} NH\text{——}CO \\ | \quad\quad | \quad /Cl \\ CO \quad\quad C< \quad . H_2O. \\ | \quad\quad | \quad \backslash Cl \\ NH\text{——}CHOH \end{array}$$ —This compound
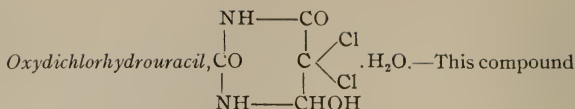
was prepared by dissolving uracil in an excess of strong chlorine water, or by oxidizing uracil with potassium chlorate and dilute hydrochloric acid. Five grams of finely pulverized uracil were suspended in about 100 cc. of chlorine water and chlorine gas conducted into the solution until the pyrimidine had dissolved. The excess of chlorine was then removed with a current of air and the solution concentrated on the steam bath. On cooling, prismatic crystals of chloruracil (see below) deposited. These were removed by filtration and the filtrate concentrated further. The hydropyrimidine then separated, on cooling, in the form of tables melting at 205°–208° with effervescence. In a second experiment 2 grams of uracil were dissolved in 80 cc. of 20 per cent hydrochloric acid and the solution heated to 70°–90°. Potassium chlorate was then occasionally added in small portions and the oxidation continued at 50°–60° for four hours. The excess of chlorine was then removed in the usual manner and the solution allowed to stand. The oxydichlorhydrouracil finally separated in stout prisms which decomposed at 208°–210°. The hydropyrimidine crystallized from water in large, well-developed prisms melting at 212°–215° with effervescence. Aqueous solutions of the pyrimidine gave a purple precipitate when warmed with a solution of barium hydroxide. The pyrimidine was recovered unaltered after boiling with alcohol for 24 hours. The corresponding dibrom derivative[1] is converted into 5-bromuracil by the same treatment. Oxydichlorhydrouracil contained one molecule of water of crystallization which was determined by heating for one hour at 100°–110°.

0.9157 gram of substance lost 0.0778 gram of H_2O.

	Calculated for $C_4H_4O_3N_2Cl_2.H_2O$.	Found.
H_2O	8.30	8.49

Nitrogen determination for hydrous pyrimidine (Kjeldahl):

	Calculated for $C_4H_4O_3N_2Cl_2.H_2O$.	Found.
N	12.90	12.67

[1] Wheeler and Johnson: J. Biol. Chem., **3**, 183.
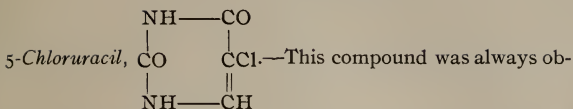
$$\begin{array}{ccc} NH & \!\!\!\!-\!\!\!- & CO \\ | & & | \\ \text{5-}\textit{Chloruracil,} \quad CO & & CCl. \\ | & & \| \\ NH & \!\!\!\!-\!\!\!- & CH \end{array}$$ —This compound was always ob-

tained associated with oxydichlorhydrouracil when uracil was
treated with chlorine water. It can be prepared by reducing
the hydropyrimidine with tin and hydrochloric acid. The pyrimi-
dine separated from the acid solution in the form of rectangular
prisms and square tables. It was practically insoluble in alco-
hol and cold water. It crystallized from hot water in prisms
melting at 300°–305° according to the rate of heating. The
pyrimidine did not contain water of crystallization. Nitro-
gen (Kjeldahl):

	Calculated for $C_4H_3O_2N_2Cl$.	I.	Found. II.	III.
N	19.11	19.03	19.5	19.00
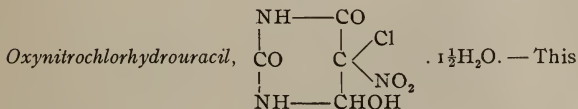
$$\begin{array}{ccc} NH & \!\!\!\!-\!\!\!- & CO \\ | & & | \;\diagup Cl \\ \textit{Oxynitrochlorhydrouracil,} \quad CO & & C \!\!<\!\! \\ | & & | \;\diagdown NO_2 \\ NH & \!\!\!\!-\!\!\!- & CHOH \end{array}$$. $1\frac{1}{2}H_2O$. — This

pyrimidine was prepared by dissolving 1.0 gram of 5-chlor-
uracil in 10 cc. of fuming nitric acid (sp. gr. 1.5). When the
solution was allowed to evaporate spontaneously, in the at-
mosphere, the pyrimidine separated in hard, prismatic crys-
tals. The substance had no definite melting point but de-
composed with effervescence from 150° to 160°, according to
the rate of heating. It slowly underwent decomposition
when heated at 100°–110° and was also decomposed by boil-
ing water. The compound contained water of crystalliza-
tion (Analysis I.), which it slowly lost when exposed to the
atmosphere. After drying over sulphuric acid, in a desicca-
tor, for 6 days, the analytical determination agreed with the
calculated value for the anhydrous material (Analyses II.
and III.). (Kjeldahl):

	Calculated for $C_4H_4O_5N_3Cl.1\frac{1}{2}H_2O$.	Found. I.	
N	17.75	17.7	

	Calculated for $C_4H_4O_5N_3Cl$.	Found. II.	III.
N	20.04	19.57	19.6

Oxychlorbromhydrouracil,

$$\begin{array}{c} NH\!\!-\!\!CO \\ | \quad\quad | \quad Cl \\ CO \quad\; C\!\!<\!\! \\ | \quad\quad | \quad Br \\ NH\!\!-\!\!CHOH \end{array} . H_2O. \text{—This pyr-}$$
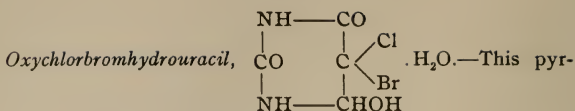
imidine can be prepared from 5-bromuracil or 5-chloruracil by dissolving them in an excess of chlorine water and bromine water, respectively. It was very soluble in water and crystallized from bromine water in prismatic crystals, decomposing at 195°–200°, with effervescence. It reacted with barium hydroxide, in aqueous solution, giving a purple precipitate. The pyrimidine contained one molecule of water of crystallization, which was determined by heating for one hour at 90°–110°. The compound slowly loses its water of crystallization in the atmosphere and becomes anhydrous after standing for several hours in a desiccator over sulphuric acid.

    I. 0.7413 gram substance lost 0.0516 gram H_2O.
    II. 0.2029 gram substance lost 0.0123 gram H_2O.

	Calculated for $C_4H_4O_3N_2ClBr.H_2O$.	Found. I.	II.
H_2O	6.88	6.95	6.50

Nitrogen determination for hydrous pyrimidine (Kjeldahl):

	Calculated for $C_4H_4O_3N_2ClBr.H_2O$.	Found.
N	10.70	10.66

Nitrogen determination for anhydrous pyrimidine (Kjeldahl):

	Calculated for $C_4H_4O_3N_2ClBr$.	Found. I.	II.
N	11.49	11.31	11.4

Action of Boiling Alcohol on Oxychlorbromhydrouracil.—Five-tenths of a gram of the hydropyrimidine, melting at 195°–200°, was dissolved in 20 cc. of absolute alcohol and the solution boiled for ten hours. The alcohol was then removed by evaporation and the product obtained was crystallized from hot water. It separated in stout prisms, decomposing at 300°–305°. It gave a test for chlorine and a mix-

ture of the compound and 5-chloruracil decomposed sharply at 300°–305°.   Analysis (Kjeldahl):

	Calculated for $C_4H_3O_2N_2Cl$.	Calculated for $C_4H_3O_2N_2Br$.	Found.
N	19.11	14.66	19.04

Action of Bromine Water on 5-Iodouracil.—5-Iodouracil was decomposed by bromine water with liberation of iodine.   About 1 gram of the pyrimidine was dissolved in bromine water, and the solution allowed to evaporate spontaneously in the atmosphere.   Transparent prisms finally separated, which decomposed sharply at 200°–205°.   The compound did not contain iodine, but gave a strong test for bromine.   It was converted into 5-bromuracil when heated with absolute alcohol. A nitrogen determination agreed with the calculated value for oxydibromhydrouracil[1] (Kjeldahl):

	Calculated for $C_4H_4O_3N_2Br_2$.	Found.
N	9.72	9.6

The Action of Nitric Acid on Thymine.

Nitric Acid (sp. gr. 1.415).—Five-tenths of a gram of thymine was dissolved in 2 cc. of concentrated nitric acid and the solution evaporated to dryness on the steam bath.   There was no evidence of any reaction and the thymine was recovered unaltered.   It deposited from hot water in plates that decomposed at about 321°.   When mixed with pure thymine this decomposition point was not lowered.

Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.23

Nitric Acid (sp. gr. 1.5).   The Formation of α-Oxynitrohydrothymine,

$$\begin{array}{c} NH\text{——}CO \\ | \qquad | \qquad CH_3 \\ CO \qquad C\!\!<\!\! \\ | \qquad | \qquad NO_2 \\ NH\text{——}CHOH \end{array}$$
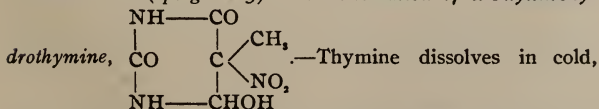
.—Thymine dissolves in cold, fuming nitric acid with slight evolution of heat.   If red fumes are evolved by this treatment it is a safe indication that the

[1] Wheeler and Johnson: *Loc. cit.*

thymine is not pure. The hydropyrimidine was obtained perfectly pure, and the yield was quantitative, when thymine was treated with fuming nitric acid under the following conditions: One gram of thymine was dissolved in 6 cc. of nitric acid and the solution allowed to evaporate at ordinary temperature. The nitro derivative deposited in large, well-developed prisms or blocks, which decrepitated above 130° and melted at 183° with violent effervescence. The compound was soluble in hot water, extremely soluble in alcohol, and separated from both these solvents in blocks that melted at 183°–185°. It was practically insoluble in benzene. The pyrimidine did not lose weight after heating for 1.5 hours at 100°–110° and again for one-half hour at 110°–115°. When heated above 120° it slowly underwent decomposition. The composition of the compound was not altered by recrystallization from absolute alcohol (Analysis III.).

0.2086 gram substance gave 0.2454 gram CO_2 and 0.0695 gram H_2O.

Nitrogen (Kjeldahl):

	Calculated for $C_5H_7O_5N_3$.	Calculated for $C_5H_6O_2N_2$.	I.	Found. II.	III.
C	31.74	47.61	32.08	. . .	. . .
H	3.70	4.76	3.70	. . .	. . .
N	22.22	22.22	. . .	22.00	21.95

α-Oxynitrohydrothymine dissolves in water, giving an acid reaction. The pyrimidine undergoes decomposition when its aqueous solution is boiled. The addition of barium hydroxide to its aqueous solution produces no precipitate or color; also no thymine deposited when an alcoholic solution of the pyrimidine was treated with ammonia. When the nitropyrimidine was dissolved in concentrated sulphuric acid, and a few drops of ferrous sulphate solution were added, the characteristic test for nitric acid was obtained. α-Oxynitrohydrothymine can also be prepared by dissolving thymine in fuming nitric acid (sp. gr. 1.5) and evaporating the solution to dryness, at once, on the steam bath. This method of nitration can be recommended for preparing quickly small quantities of the hydropyrimidine. The yields are not quan-

titative, since part of the thymine undergoes oxidation. The best results are obtained when 1 gram portions are nitrated under the following conditions: One gram of thymine is dissolved in 4 cc. of nitric acid (sp. gr. 1.5) and the solution evaporated to dryness as quickly as possible. The nitrothymine is obtained as a colorless, crystalline residue which separates from water in blocks decomposing at 183°–185°. It is possible, in this manner, to prepare several grams of the hydropyrimidine in a few minutes. The yields obtained by this method of nitration were very uniform and are given in the table below.

Number.	Nitric acid, sp. gr. 1.5. Cc.	Weight of thymine. Grams.	Weight of crude oxynitrohydrothymine. Grams.	Weight of hydropyrimidine after 1 crystallization from water. M.p. 183°–185°. Grams.	Per cent of theoretical of pure hydrothymine.
1	4	1	1.1	0.80	57.1
2	4	1	1.1	0.82	58.5
3	4	1	1.1	0.79	56.4
4	4	1	1.1	0.81	57.8
5	8	2	2.15	1.60	55.5
6	4	1	1.2	0.90	64.4
7	8	2	2.1	1.50	53.5

Crystallography of Oxynitrohydrothymine.

By W. E. FORD.

The pyrimidine crystallizes in the triclinic system, showing a combination of b (010), c (001), a (100), M (110), d (034) and X (111). The crystals were small, averaging about 2 mm. broad by 1 mm. thick. In habit they present the appearance of diamond-shaped tables with beveled edges, as is illustrated in the figure. The face, b (010), is always the most prominent, while the prism with the pinacoid, a, and the base with the dome, d, form the beveling faces. Frequently one of these latter faces is much subordinated in size, or may be entirely wanting. The negative pyramid, X, is always small, and often not present. The crystal faces, although distinct to the eye, were very poorly adapted for measurement with

the reflection goniometer. They were usually quite rough or curved and gave indistinct and broad signals on the goniometer. A series of the crystals was measured on the two-circle goniometer, and the average of the best readings ob-

tained was taken for the fundamental angles, but the angles as given and the crystallographic constants calculated from them can be considered only as proximate. The measured angles were as follows:
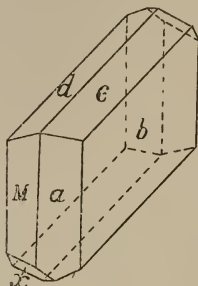
(010) : (110) = 63°54′.
(010) : (100) = 96°15′.
(010) : (001) = 73°38′.
Zone (010) . (110) : Zone (010) . (001) = 79°35′.
Zone (010) . (110) : Zone (010) . (101) = 50°5′.
(010) : (034) = 71°33′; calc. = 71°46′.

Using the first five measurements as fundamentals, the crystal constants were calculated to be

$$a : b : c = 0.578 : 1.000 : 0.420. \quad \alpha = 107°35′, \beta = 100°25′,$$
$$\gamma = 80°59′.$$

The crystals show a good cleavage parallel to *c* (001). On account of the nature of the material only a few of the optical facts concerning the compound could be determined. It possesses a strong double refraction. The extinction direction on *b* (010) is inclined to the edge between *b* and *a* at 31°. The crystals, when looked at in the polariscope in a direction

perpendicular to *c* (001), the cleavage face, show the emergence of an optic axis nearly in the center of the field.

Action of Nitric Acid (*sp. gr. 1.5*) *in Presence of Concentrated Sulphuric Acid.*—There was an immediate reaction, with evolution of red fumes, when 0.5 gram of thymine was dissolved in a mixture of 3 cc. of nitric and 3 cc. of sulphuric acids. When the mixture was allowed to stand, without cooling, the reaction continued to increase in violence, with evolution of heat, and the thymine was completely decomposed. In a second experiment, 1 gram of thymine was dissolved in a cold mixture of 3 cc. nitric and 2 cc. concentrated sulphuric acids. This solution was held at a temperature of 70°–75° for about three-quarters of an hour, when gas bubbles had practically ceased to be formed. The acid solution was then cooled and poured into 15 cc. of ice water. After standing for several hours, stout, well-developed prisms deposited from the solution. They melted at 183°–185°, with effervescence, and were identified as *oxynitrohydrothymine*. They were soluble in alcohol and warm water. Analysis (Kjeldahl):

	Calculated for $C_5H_7O_5N_3$.	Found.
N	22.22	21.66

Action of Bromine Water on α-Oxynitrohydrothymine.—One gram of the hydropyrimidine was dissolved in an excess of bromine water and the solution allowed to evaporate spontaneously. There was no evidence of a reaction and oxynitrohydrothymine separated in large, transparent blocks melting at 183°–185°.

Analysis (Kjeldahl):

	Calculated for $C_5H_7O_5N_3$.	Found.
N	22.22	22.42

Reduction of α-Oxynitrohydrothymine with Aluminum Amalgam.—Two and five-tenths grams of the hydrothymine were dissolved in cold water and reduced for 1.5 hours with an excess of aluminum amalgam. The temperature was not allowed to rise above 40° during the reduction. After fil-

tering from aluminum amalgam and aluminum hydroxide the filtrate was evaporated to dryness. I obtained a crystalline deposit which was difficultly soluble in cold water, but separated from hot water in plates melting at 320°. When mixed with thymine the melting point was not lowered. It dissolved in fuming nitric acid, giving the original *α-oxynitrohydrothymine* melting at 183°–185°. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.01

Reduction of α-Oxynitrohydrothymine with Tin and Hydrochloric Acid.—Two and two-tenths grams of the hydropyrimidine were reduced for one hour with an excess of tin and concentrated hydrochloric acid. The acid solution was then evaporated to dryness, the residue dissolved in water, and the tin removed by precipitation with hydrogen sulphide. When the aqueous filtrate was concentrated and cooled, thymine separated in glistening plates, decomposing at 320°. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.10

$$\beta\text{-}Oxynitrohydrothymine,\quad \begin{array}{c} HH{-\!\!-}CO \\ | \quad\quad | \quad CH_3 \\ CO \quad\; C{\Big\langle} \\ | \quad\quad | \quad NO_2 \\ NH{-\!\!-}CHOH \end{array}\quad.\;-\text{I have per-}$$
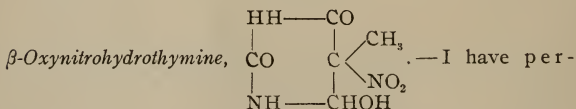
formed fifteen experiments, during this research, to determine the behavior of fuming nitric acid towards thymine under different conditions. I have taken different amounts of thymine (0.5–5.0 grams), and have varied the proportions of nitric acid. I have also allowed the acid solution to evaporate under different conditions—at room temperature, on the steam oven, in a vacuum over sulphuric acid, and at 100°—but in only two experiments have I observed the formation of *β-oxynitrohydrothymine*. The conditions under which I obtained this isomer were as follows: One and six-tenths grams of thymine were dissolved in 8 cc. of cold, fuming nitric acid (sp. gr. 1.5) and the solution was allowed to evaporate

in the atmosphere overnight. The following morning large, transparent blocks had deposited, which showed no signs of melting at 183°–185°, but decomposed at 230°–235°, according to the rate of heating. One of the crystals selected for analysis weighed 0.2600 gram. The isomer did not revert to the α derivative when crystallized from water or absolute alcohol, but separated, on cooling, in well-developed prisms decomposing at 230°–236°. In another experiment, 0.5 gram of thymine was dissolved in 10 cc. of fuming nitric acid and the solution allowed to evaporate over sulphuric acid in a vacuum desiccator. I obtained practically a quantitative yield of the β derivative melting at 230°-235°. The compound did not lose weight when heated for one-half hour at 90°–100°. Analysis (Kjeldahl):

	Calculated for $C_5H_7O_5N_3$.	I.	Found. II.
N	22.22	22.00	22.1

Reduction of β-Oxynitrohydrothymine with Tin and Hydrochloric Acid.—This compound was reduced in the same manner as the α derivative. The excess of tin was removed with hydrogen sulphide and the filtrate evaporated to dryness. I obtained a crystalline residue which separated from water in plates melting at 315°–320°. The compound sublimed when heated in a test tube, and when mixed with thymine, the melting point was not lowered. It dissolved in fuming nitric acid, giving *α-oxynitrohydrothymine* melting at 183°–185°. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.31

Rearrangement of β-Oxynitrohydrothymine into α-Oxynitrohydrothymine.—Some of the α-pyrimidine, melting at 183°–185°, was preserved in a desiccator from May 29, 1907, until January 17, 1908. It apparently underwent no change, and melted at 181°–183° with effervescence. A sample of the β-pyrimidine, melting at 230°–235°, was preserved from June 19, 1907, to October 7, 1907. It then decomposed at 227°–235°, and a nitrogen determination (Kjeldahl) gave 22.00

per cent; calculated, 22.22 per cent nitrogen. This material was not examined again until January 16, 1908. It then had completely rearranged to the α-pyrimidine and melted at 183°–188° with effervescence. A mixture of this material and pure α-oxynitrohydrothymine melted at 183°–186° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_5H_7O_5N_3$.	Found.
N	22.22	21.9

I take pleasure in thanking Professor W. E. Ford for the crystallographic description of oxynitrohydrothymine and also Mr. D. B. Jones for his help in this investigation.

NEW HAVEN, CONN.,
Jan. 18, 1908.

THE "SYN" AND "ANTI" STEREOISOMERISM OF NITROGEN COMPOUNDS.

By JULIUS STIEGLITZ.

In 1903,[1] in the course of an investigation with R. B. Earle on the cause of the rearrangement of the metal salts of acid chlor- and bromamides, RC(: N Hal)OMe, a long search for stereoisomeric esters, RC(N: NCl)OR', corresponding in structure to the above salts, resulted in the discovery of the first known pair of such stereoisomers in the form of two methyl chlorimido-*m*-nitrobenzoates, $NO_2C_6H_4C$(: NCl)OCH_3$. The investigation of such stereoisomers has been continued since then by myself in collaboration with W. J. Hale, Oscar Eckstein, and Willis S. Hilpert; the conclusions drawn in the preliminary report have been confirmed in every detail and a large amount of additional evidence obtained, supplementing the results obtained in the first place. In a later paper the work done with the stereoisomeric esters on the question of the theory of the "Beckmann rearrangement" will be discussed; in this paper it is intended to consider only the question of the new class of stereoisomers, whose existence has

[1] THIS JOURNAL, **30**, 399 (1903).

been fully established, and their relation to the general question of stereoisomerism of nitrogen compounds.

I. Stereoisomeric Chlorimidoesters.

The following pairs of stereoisomeric chlorimidoesters have now been prepared in this laboratory, the physical and chemical differences of the two compounds forming each pair being briefly summarized:

1. α- and β-Methyl chlorimido-m-nitrobenzoates,[1]

$$NO_2C_6H_4C—OCH_3 \quad and \quad NO_2C_6H_4C—OCH_3$$
$$\underset{Cl—N}{\|} \qquad\qquad \underset{N—Cl}{\|} \quad,$$
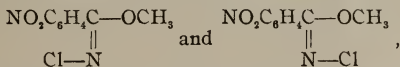
were prepared with Earle and are described in the preliminary report. Hilpert[2] has improved the method of preparation and of separation of the two bodies, so that they are now very easily obtained. The α compound forms needles melting at 88° and is less soluble in chloroform and ligroin than is the β compound. It does not lose its identity when subjected to the various forms of physical transformation; recrystallization from various solvents, fusion and solidification, moderate heat (150°), do not change it into the other form. Under the influence of dry chlorine (see IV., below) it is transformed into the more stable β compound.

The β compound forms thick prisms melting at 84°, is much more soluble in ligroin and chloroform than the α body, and also preserves its identity through all forms of physical changes. It is much the more stable of the two stereoisomers, is formed in larger proportion, and is obtained from the α body by the action of chlorine, as stated above; but the β compound is also transformed by the same agent to a slight extent into the α compound, the reaction being reversible, as proved by Dr. Hilpert.

A mixture of equal quantities of the two pure stereoisomers melts at 63°–65°, the melting point being depressed some 20°.

[1] The prefix *a* was uniformly given to the higher melting stereoisomer. See below, Part V., in regard to the configurations of the compounds.

[2] A report by Dr. Hilpert will appear in a later number of THIS JOURNAL. I wish to take this occasion to thank Dr. Hilpert, my chief collaborator in the study of these stereoisomers, for his thorough and skilful work.

2. α- and β-Ethyl chlorimido-m-nitrobenzoates,
$NO_2C_6H_4C(:NCl)OC_2H_5$, were prepared with Dr. Hale. The α compound, crystallizing in long, flat needles and melting at 63°, is formed in largest quantity and is the more stable of the two stereoisomers, in contrast to the relations for the methyl esters. In all other respects it resembles the α compound of the methyl ester pair. The β compound crystallizes in small, striated prisms, melts at 52°, and is formed in very small quantities. Dry chlorine converts it into the α body.

3. α- and β-Methyl chlorimido-p-nitrobenzoates,
$p\text{-}NO_2C_6H_4C(:NCl)OCH_3$, were prepared by Hilpert,[1] as were all the succeeding stereoisomers. The α compound resembles the α compound of the meta series in its appearance, stability, and behavior; it forms needles melting at 99°–100°. The β form appears as thick prisms, melts at 76°, is the more soluble and the more stable stereoisomer of the two. Chlorine converts the α compound readily into the β form, but the latter is also to some extent converted into the less stable α form by the same agent. A mixture of the two stereoisomers melts at about 60°.

4. α and β- Ethyl chlorimido-p-nitrobenzoates,[1]
$p\text{-}NO_2C_6H_4C(:NCl)OC_2H_5$, are entirely analogous to the stereoisomeric *ethyl* esters of the meta series—particularly also in regard to the striking fact that here again the α compound (needles, m. p. 96°) is so much the more stable that the β body (plates, m. p. 90°) could be obtained (0.5 gram) only by weeks of patient collecting of single crystals. A mixture of the two bodies melts at about 72°.

5. α- and β-Methyl m-Nitro-p-methylbenzoates,[2]
$m\text{-}NO_2\text{-}p\text{-}CH_3C_6H_3C(NCl)OCH_3$.—The higher melting α compound (m. p. 84°–85°) forms plates, is the less soluble, but also the less stable, isomer, forming the β compound under the influence of chlorine. The β compound forms needles, which melt at 71°, and is the more stable form. A mixture of the two melts at 53°–54°. Except for the noteworthy change of crystal forms, the two stereoisomers conform en-

[1] *Loc. cit.*
[2] *Ibid.*

tirely in their properties to the corresponding α and β compounds of the other stereoisomeric *methyl* esters.

6. *α- and β-Methyl Chlorimido-β-naphthoates*,[1] β-$C_{10}H_7C(NCl)OCH_3$.—All the stereoisomers hitherto described have been nitro derivatives, the nitro group being used to raise the melting points of the esters and to facilitate somewhat their separation by fractional crystallization. The chlorimidoesters of β-naphthoic acid were prepared in the hope that they would also be solid and that we could isolate stereoisomers which would have no nitro group in the molecule. This hope was realized. The α compound forms needles, melts at 125°, and is much the less soluble of the two. The β compound forms thin plates melting at 72°. A mixture of the two compounds melts at 66°–67°. There is not much difference in the stability of the stereoisomers, they can be converted one into the other by treatment with hot water.[1] They are stable towards physical changes and do not lose their identity.

7. *α- and β-Ethyl Chlorimido-β-naphthoates*,[1] β-$C_{10}H_7C(NCl)OC_2H_5$.—The α compound is the less soluble, crystallizes in thin lamellae looking like needles, and melts at 72°. The β compound was probably not isolated but its existence was rigorously proved in a compound melting at 39°, which, by analysis, represented perfectly pure ethyl chlorimidonaphthoate and for which identity of structure with that of the α body, *i. e.*, as an ethyl chlorimido-β-naphthoate, was proved.[1] The body melting at 39° is considered to be a saturated mixture of the α and β forms, because its melting point was not depressed by the addition of some pure α compound (m. p. 72°). It is certain that it contains a compound with the same composition and same structure as the α body, but different from it and therefore stereoisomeric with it.

II. The Proof of Identical Structure for each Pair of Stereoisomers.

The rigorous proof of the identity of structure for the two

[1] Hilpert: *Loc. cit.*

compounds forming each pair of stereoisomers, $RC(:NCl)OR'$,[1] was, of course, considered of prime importance, especially in view of the fact that structural isomerism in the acid radical R, in regard to the position of the substituting nitro groups, etc., and isomerism in regard to the position of the alkyl radical R' had to be excluded.

The identity of structure of the pairs of stereoisomers was in each case proved in the following direct way; each stereoisomer, its purest preparation being always used, was treated in ligroin solution with dry hydrogen chloride, reduction to the hydrochloride of the mother substance, the imidoester, being effected as follows:

$$RC(:NCl)OR' + 2HCl \longrightarrow RC(:NH_2Cl)OR' + Cl_2.$$
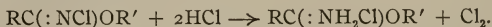
The identity of the imidoester salt formed was established in two ways: (1) The dry imidoester hydrochlorides break down, when heated, into an acid amide and an alkyl chloride, according to the formulation

$$RC(:NH_2Cl)OR' \longrightarrow RCONH_2 + R'Cl.$$

The acid amide thus obtained from each stereoisomer was not only examined in regard to its own melting point, but, the melting points of the acid amide prepared from a pair of stereoisomers being always found exactly the same, a melting point of a mixture of the two preparations was also taken and found to be the same as that of the individual amides. This evidence brought conclusive proof of the identity of the acid radical R in each pair of stereoisomers.

(2) The imidoester salts break down under the influence of water into esters and ammonium chloride, according to the formulation

$$RC(NH_2Cl)OR' + H_2O \longrightarrow RCOOR' + NH_4Cl.$$
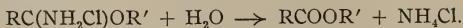
Each of a pair of stereoisomeric chlorimidoesters always gave the same acid ester (methyl *m*-nitrobenzoate, methyl *p*-nitrobenzoate, etc.), as the other one of the pair did, the identity of the ester being proved by the rigorous method described for the acid amides. This proved the identity of

[1] Hilpert: *Loc. cit.*

the groups OR' and of the acid radicals R in the pairs of stereo-isomers and completed the proof of their structure.

Corroborative evidence of the identity of the structures or the pairs of stereoisomers was found as follows: (3) For the original pair of stereoisomers, methyl chlorimido-*m*-nitro-benzoate, the isomeric compound, *m*-nitrobenzchlormethyl-amide, $NO_2C_6H_4CO(NClCH_3)$, containing the methyl group attached to nitrogen and not to oxygen, was prepared by Stieglitz and Earle and found to be different from the two stereoisomers.[1] (4) The derivatives obtained from *p*-nitro-benzoic acid are quite different in their physical constants from those obtained from *m*-nitrobenzoic acid. (5) The smooth and rapid transformation of one stereoisomer into its more stable mate by the action of chlorine or hot water (see IV.) precludes any structural difference in the groups R and R' and is exactly what is to be expected of such stereoisomers.

III. The Physical Behavior.

Molecular weight determinations by the cryoscopic method were made in benzene solution with three pairs of stereoiso-mers, the methyl chlorimido-*m*-nitrobenzoates, the methyl *p*-methyl-*m*-nitrobenzoates, and the methyl chlorimidonaph-thoates. They proved beyond cavil that the two members of a pair have the same molecular weight, the possibility of poly-merism being thus excluded.

Physical or crystal isomerism was rigorously excluded by the fact that each stereoisomer maintains its identity under all the changes of physical condition that could be applied. Although there is always a considerable difference in solu-bility, one stereoisomer could never be converted into another (*e. g.*, the less soluble modification) by means of a solvent. Fusion and subsequent solidification, in contact with its own crystals or even with the solid phase of the other form, never produced any transformation of one stereoisomer into the other. A mixture of the two forms always has a very much lower melting point than either pure form (there is a lowering sometimes of from 20° to 50°) and this low-melting mixture,

[1] *Loc. cit.*

allowed to solidify, gives the same melting point when heated again, showing that there is no change of form even under these, the most favorable conditions for the transformation of crystal modifications. Dr. Hilpert was also able to prove the persistence of the configuration and structure of the molecules of the stereoisomeric methyl chlorimido-*p*-nitrobenzoates in the gas form by distilling them at 134° under 1 mm. pressure.

IV. The Transformation, Chemically, of the Less Stable Stereoisomer into the More Stable One, and Vice Versa—a Reversible Reaction.

Reagents which are easily absorbed by unsaturated bodies, the halogens and the halogen acids, and easily given off again, have often been observed, sometimes when present only in traces, to have the power of transforming one form of the cis-trans stereoisomers of the ethylene series[1] into the other form, and the halogen acids have also been found to effect a similar transformation when acting on stereoisomeric oximes.[2] The change is supposed to be due to the addition of the reagent to the double bond causing the stereoisomerism, although the addition, at least in some cases, is not complete.[3]

For stereoisomeric chlorimidoesters it was thought that a similar transformation, especially of the less stable into the more stable form, should be effected by chlorine. Without destroying or otherwise affecting the compounds, chlorine could form unstable addition products, which, by the loss of chlorine after the opening of the double bond and a rotation of the now singly bound carbon atom, could form the other stereoisomer:

$$\begin{array}{c} \text{R—C—OR}' \\ \| \\ \text{Cl—N} \end{array} + \text{Cl}_2 \underset{\leftarrow}{\overset{\rightarrow}{\rightleftharpoons}} \begin{array}{c} \text{R—C}{<}^{\text{OR}'}_{\text{Cl}} \\ | \\ \text{Cl—N—Cl} \end{array} \underset{\leftarrow}{\overset{\rightarrow}{\rightleftharpoons}} \begin{array}{c} \text{R—C—OR}' \\ \| \\ \text{N—Cl} \end{array} + \text{Cl}_2.$$
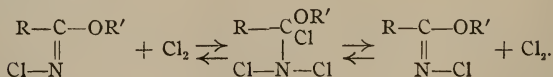
A consideration of such an action leads to the conclusion that if it takes place at all it must be reversible to a certain

[1] See Meyer and Jacobson: Organische Chemie, Vol. II, p. 685.
[2] *Ibid.*, 509.
[3] *Ibid.*, 686.

extent, producing a condition of equilibrium, since chlorine could be added and lost in either way.

Both these suppositions have been confirmed by experiment. The change of one stereoisomer into its more stable mate was first carried out with α-methyl chlorimido-*m*-nitrobenzoate, which is converted into the more stable β form by the action, for two minutes,[1] of dry chlorine at 90°. For the ethyl ester it was found that the β compound is converted into the α compound, which, in this case, is the more stable one.[2] Hilpert[3] not only used this method successfully on the stereoisomers he discovered but he also proved in the two cases tried (the α and β forms of methyl chlorimido-*m*-nitrobenzoate and the two forms of the same ester of *p*-nitrobenzoic acid) that the action is really a reversible one, the more stable form going in each case to a slight extent over into the less stable modification, which was isolated in sufficient quantity to permit of its complete identification.

Hilpert[3] has also found a second means for effecting such a reversible transformation in the boiling of the stereoisomeric methyl chlorimidonaphthoates with water; probably a trace of hypochlorous acid is formed and acts as represented for chlorine in the above equations.

In these transformations, fulfilling every anticipation based on the well-known behavior of stereoisomers of this type, we have, therefore, a final confirmation of the conclusion that the relations of the isomers we are dealing with are those of stereoisomers.

V. *The Configurations of the Stereoisomeric Chlorimidoesters.*

Little direct evidence as to which configuration belongs in each instance to the stereoisomers distinguished as α and β can be brought. Towards heat (200°), effecting, by destructive distillation, partly a "Beckmann rearrangement,"[4] partly a decomposition into nitriles, no difference in the behavior of the two stereoisomers of a pair could be detected, either

[1] This was carried out with Mr. Hale; *vide* a later report.
[2] *Ibid.*
[3] *Loc. cit.*
[4] *Vide* the later report with Hale and Eckstein.

qualitatively or quantitatively. The best evidence we have on the question of configuration is based on the relative stability of the methyl and ethyl esters, as discussed in Dr. Hilpert's report, and as the subject is not of very great moment for the argument of this paper, it will be sufficient to refer here to my young collaborator's paper for the discussion of the question.

VI. *The Stereoisomeric Chlorimidoesters and the "Syn" and "Anti" Stereoisomerism of Nitrogen Derivatives.*

The theory of Hantzsch and Werner[1] that the stereoisomerism of nitrogen derivatives containing a doubly bound nitrogen atom is of the same nature as the stereoisomerism of ethylene derivatives containing doubly bound carbon atoms has given a satisfactory and uniform basis of explanation of all the observed cases of nitrogen stereoisomers. According to their view we have the two configurations,

$$X—C—Y \qquad X—C—Y$$
$$\underset{Z—N}{\|} \quad \text{and} \quad \underset{N—Z}{\|} .$$
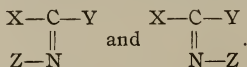
As is well-known, when the theory was first advanced, Victor Meyer,[2] the discoverer of the first proved cases of nitrogen stereoisomerism, the benziloximes and dioximes, at first opposed Hantzsch's theory and thought it possible that the difference in configuration might be due to peculiarities of the hydroxylamine molecule; and Hantzsch himself said at the time:[3] "In spite of all the facts being in favor then of the first configurations"—(Hantzsch's, as given above)—"they do not, also according to our own opinion, contain the definite proof of the theory. This proof would only be brought when the behavior of hydroxylamine should no longer be found exceptional and cases of stereoisomerism for other nitrogen derivatives of the general form $XYC:NZ$ than the oximes should be discovered." The discovery by Hantzsch, then, of the stereoisomeric phenylhydrazones brought the evidence that hydroxylamine was not unique among nitrogen compounds.

[1] Ber. d. chem. Ges., **23**, 11, 1243 (1890).
[2] *Ibid.*, **16**, 503 (1883), etc.
[3] *Ibid.*, **24**, 3515 (1891).

in producing stereoisomers, and Hantzsch and Werner's theory has secured a well-merited general acceptance and has proved its usefulness, particularly also in the case of diazo derivatives.

Nevertheless, it has remained a fact, as far as we can discover,[1] that all efforts to produce unquestioned stereoisomers of the above type from amine derivatives other than hydroxylamine and hydrazine, in which Z (in the above structure) is a simple radical, such as phenyl or carbethoxyl, etc., have remained hitherto without result, even in the extended investigations carried out, up to a recent date, under the direction of the creator of the above theory.[2] In the few cases we have found in the literature, in which, for instance, stereoisomeric aniline derivatives were supposed to have been obtained, structural isomerism, especially, and physical isomerism and polymerism have not been rigorously excluded,[3] so that these compounds have never been accepted as unquestioned representatives of stereoisomerism among nitrogen derivatives. On the other hand, the decided chemical similarity between hydroxylamine and hydrazine has made it desirable to discover stereoisomers in no wise connected with the oxime and hydrazone class of compounds. To this fact, the search for derivatives in which Z would be some simple carbon radical has been largely due.

The newly discovered stereoisomeric chlorimidoesters, therefore, fill, we believe, a long felt gap in the experimental development of Hantzsch and Werner's theory. In this case, Z assumes the simplest possible form—a single chlorine atom—and a proof of stereoisomerism, excluding structural isomerism, polymerism, and physical isomerism, has been possible by rigorous methods of organic and physical chemistry.[4]

[1] See, for instance, Hantzsch: Stereochemie (1904), p. 141; Ber. d. chem. Ges., **34,** 822 (1901).

[2] Ber. d. chem. Ges., **24,** 3518 (1891); **26,** 9 (1893); **26,** 926 (1893); **28,** 977 (1895); **30,** 3003 (1897); **34,** 822 (1901).

[3] *Vide* Meyer and Jacobson's criticism: Organische Chemie, II, p. 509; and Hantzsch's: Ber. d. chem. Ges., **34,** 822 (1901); and Hantzsch's Stereochemie (1904), p. 141. Also, Meyer and Jacobson's Organische Chemie, 2d Edition, I, p. 785 (1906).

[4] The work on this type of stereoisomers is being continued. Mr. Raiford is trying to obtain stereoisomeric quinonechlorimides and Mr. Rosario del Valdeczo is working on the possibility of isolating stereoisomeric imidoesters. Mr. Peterson is working on stereoisomeric chlorimidoketones and we have evidence of the existence of two chlorimido-*p*-chlorbenzophenones.

Their existence is in complete agreement with Hantzsch and Werner's fundamental hypothesis.

INVESTIGATION OF THE CLAISEN CONDENSATION. II. A CONTRIBUTION TOWARDS THE ELUCIDATION OF THE MECHANISM OF THE REACTION.

BY J. BISHOP TINGLE AND ERNEST E. GORSLINE.

THEORETICAL.

The Effect on the Reaction of Varying Conditions.

In our previous paper on this subject[1] we have presented evidence which proves that ether, pyridine, and quinoline act as catalytic agents in promoting the Claisen condensation between certain ketones and esters, in the presence of sodium. The present communication describes a considerable number of experiments which we have carried out for the purpose of determining the influence on the reaction and, therefore, on the yield of diketone of changes in the conditions. That such changes may exert a marked influence was shown some years ago by J. Bishop Tingle[2] in the case of camphoroxalic acid. We have studied the effect of variation of the temperature and of the solvent, and also the result of employing, as condensing agents, such substances as sodium, sodamide, and calcium. We have also carried out a few experiments with sodium ethylate free from alcohol and with sodium ethylate in absolute alcoholic solution. The last two reagents named have been used frequently by Claisen[3] and many other chemists, and the employment of metallic sodium is, of course, quite common. It is believed that the use of metallic calcium in this connection is new.

A. The Use of Calcium and Sodamide as Condensing Agents. —Camphor and the ethyl esters of oxalic, benzoic, and cinnamic acids have been condensed, using calcium and sodamide

[1] THIS JOURNAL, **37**, 483 (1907).

[2] *Ibid.*, **19**, 393 (1897).

[3] Ber. d. chem. Ges., **38**, 709.

as the condensing agents. The temperature and solvent employed were also varied in each case. The results show that with camphor as the ketone, metallic calcium and sodamide are practically useless as condensing agents unless alcohol is added to the materials employed. Even then, the reaction must be carried out at a relatively high temperature. Under these conditions a fair yield may be obtained. This is quite different from the results recorded by Claisen,[1] who worked with sodamide, using acetone and acetophenone with ethyl acetate, and acetone with ethyl benzoate. It furnishes an illustration of the weighty influence exercised on the reaction by the nature of the ketone or aldehyde, and also by that of the ester.

Another matter of some importance and interest which this part of the work has demonstrated concerns the nature of the "solvent product" (*vide* p. 60). In the case of condensations between camphor and ethyl oxalate, in the presence of sodium, considerable quantities of camphoroxalic acid can be extracted from it.[2] The same is true when sodamide is used as the condensing agent, and also when this substance or sodium is brought into reaction with camphor and ethyl cinnamate. The results with calcium are in sharp contrast with this. In no single case has a trace of the condensation product been detected in the "solvent product." The difference may, of course, be due to the different solubilities of certain sodium or calcium compounds formed during the reaction.

B. The Effect of Sodium Ethylate upon the Condensation.— The addition of a mere trace of alcohol, or of a solution of sodium ethylate in absolute alcohol, to the mixture of ketone, ester, sodium, and solvent starts a reaction very quickly, but the yield of the diketone is always greatly reduced. The important bearing of this fact upon one of the theories concerning the mechanism of the reaction will be discussed later.

C. The Effect of Various Solvents and Temperatures.—This factor has already been discussed in our previous communication.[3] Some additional experiments have been performed

[1] Ber. d. chem. Ges., **38,** 695 (1905).
[2] J. Bishop Tingle: THIS JOURNAL, **19,** 393 (1897).
[3] THIS JOURNAL, **37,** 483 (1907).

which confirm the conclusion that practically no difference
is made in the final result by the use of any one of the follow-
ing solvents: petroleum ether (b. p. 36°), ligroin (b. p. 50°–
55°), hexane (b. p. 90°), benzene, toluene, xylene. As a
rule the condensation proceeds more slowly in these media
than it does in ethereal solution. In the case of some esters
or ketones, however, the tendency to react is so great that
variation of the solvent is without apparent effect on the
velocity of the reaction or on the yield of diketone produced.

The effect of changing the temperature was also dealt with
in our previous paper,[1] and some additional experiments con-
firm the results obtained. In general, under similar condi-
tions, the influence of the factors temperature and time are,
roughly, inversely proportional. Moreover, better yields of
diketone are obtained with higher- than with lower-boiling
solvents, provided, of course, the temperature is not suffi-
ciently great to decompose the products of the reaction.

*D. The Influence of the Constitution of the Ester upon the
Condensation.*—On account of a delay in receiving a shipment
of materials the work in this connection is much less com-
plete than could be wished. The compounds employed may
be classified as follows:.

A. Aliphatic Series: Esters of formic, acetic, butyric,
oxalic, malonic, and succinic acids.

B. Aromatic Series: Esters of benzoic, nitrobenzoic, cin-
namic, and phthalic acids.

To obtain the condensation products when the above esters
are allowed to react with camphor, it is generally necessary
to extract with ether the acidified aqueous solution obtained
by pouring the condensation product into ice water and re-
moving the solvent layer. In a few cases the product will
precipitate upon acidulation. Claisen[2] obtained oxymethyl-
enecamphor in this way and the product of the ethyl phthalate-
camphor condensation precipitates upon acidulation. By
extracting with ether, every product, including the two above
mentioned, is obtained in the form of a heavy, reddish brown

[1] *Loc. cit.*
[2] Bishop, Claisen, and Sinclair: Ann. Chem. (Liebig), **281,** 328.

oil. J Bishop Tingle[1] obtained camphoroxalic acid by the hydrolysis of the oil obtained by condensing camphor and ethyl oxalate. By the hydrolysis of the ether extract of the ethyl formate-camphor condensation Claisen's oxymethylene-camphor can be obtained. During this investigation compounds analogous to these have been isolated from the condensation of camphor with ethyl benzoate and with ethyl phthalate. No attempt has been made to purify the products obtained from the condensation of all of the above-named esters with camphor, this being beyond the scope of this investigation. It seems practically certain, from the results which have been accumulated, that these products are compounds similar in nature to camphoroxalic acid and oxymethylenecamphor. Enough work has been done, however, to show that their preparation in large quantities and in a pure form presents serious difficulties.

The experimental evidence shows that the reaction is markedly influenced by the nature of the ketone or aldehyde employed, and also by that of the ester. There is reason to doubt whether this influence is confined to a variation in the velocity. In some cases, at least, it seems to extend to the actual mechanism of the reaction. An effort has been made to obtain light on this point by a systematic study of the effect produced by variation in the constitution of the ester.

Until more work has been done on this subject it would be premature to generalize. It appears, however, that the readiness with which the reaction takes place is increased by the proximity of two carbethoxy groups. There is some evidence, which will be presented later, indicating the possibility that the mechanism of the reactions resulting in the formation of diketones is different in the case of the aliphatic and the aromatic esters.

E. The Catalytic Effect of Ether and the Tertiary Bases in the Claisen Condensation, and also in the Formation of the Grignard Reagent.—In a previous paper[2] we were able to show that ether acts as a powerful catalytic agent in promoting

[1] Inaug. Diss., Munich, 1889.
[2] *Loc. cit.*

the Claisen condensation, and that this property is shared by pyridine and quinoline. There is, thus, a complete analogy between the Claisen and the Grignard reactions.

A similar catalytic action of ether has been observed in one or two other cases. Prof. A. Michael has been good enough to point out to us that Menschutkin[1] was probably the first to show that the addition of ethyl iodide to trimethylamine takes place 200 times faster in ether than in ligroin. Freer,[2] from his experiments with sodium and acetone, which do not react except in the presence of a solvent of the latter, concludes that "ether is not an indifferent solvent."

F. The Action of Ether and the Tertiary Bases on the Aceto-acetic Ester Synthesis.—As is well known, ethyl acetoacetate is formed by condensing two molecules of ethyl acetate with one atom of sodium, using an excess of the ester as the solvent. The statement has been made by Higley[3] that in the presence of a solvent there is no trace of acetoacetic ester formed. Bacon,[4] on the other hand, whose results Higley claims to have confirmed, admits that traces of acetoacetic ester were obtained when ten parts of ether were used as a solvent.

In an interesting series of papers by Bouveault and Locquin,[5] evidence is presented to show that, while ethyl aceto-acetate is formed by the condensation of ethyl acetate and sodium when an excess of the ester is used as a solvent, when dissolved in benzene or ether the reaction results in the formation of the compound $CH_3COCH(OH)CH_3$, after treating the product of the reaction with water. Similar compounds were also obtained by condensing esters of the higher aliphatic acids with sodium.

We have carried out some experiments on the acetoacetic ester condensation, using as solvents small quantities of ether, petroleum ether (b. p. 36°), and pyridine. The catalytic effect of ether and pyridine on the velocity of the reaction is appar-

[1] J. Chem. Soc., **54**, 901 (1888); Z. physik. Chem., **6**, 41 (1890).
[2] This Journal, **15**, 582 (1893); Bacon and Freer: *Ibid.*, **38**, 367 (1907).
[3] This Journal, **37**, 293.
[4] *Ibid.*, **33**, 77–80.
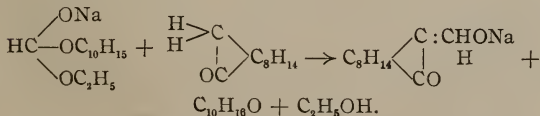[5] Bull. Soc. Chim. **36**, 629.

ent. Moreover, when purifying the product in the manner described by Gattermann,[1] there is obtained in each case a small amount of liquid which boils at 175° to 177° and gives an intense coloration with ferric chloride. The statement that no acetoacetic ester is formed in the presence of a solvent would seem to require verification. Furthermore, a long series of experiments fails to show that ether or the tertiary bases have any catalytic action when sodium reacts with esters to form compounds of the class $\begin{array}{c} C_6H_5CONa \\ \| \\ C_6H_5CONa \end{array}$. This would necessarily be the case here if only a compound of the above nature was formed.

It seems probable that the two reactions take place simultaneously, and that in the presence of solvents the reaction

$$2CH_3COOC_2H_5 + 4Na \rightarrow \begin{array}{c} CH_3CONa \\ \| \\ CH_3CONa \end{array} + 2NaOC_2H_5 \text{ is by far}$$

the preponderating one.

G. The Mechanism of the Reaction.—The Claisen condensation is explained by its discoverer as follows:[2] When camphor and ethyl formate are condensed by means of sodium wire, sodium borneolate and sodium camphor, $C_8H_{14}\begin{array}{c} CH \\ \| \\ CONa \end{array}$, are first formed, and the latter, with the ester, yields the ortho compound, $HC \begin{array}{c} ONa \\ -OC_{10}H_{15} \\ OC_2H_5 \end{array}$. This hypothetical intermediate product then reacts with camphor:

$$HC \begin{array}{c} ONa \\ -OC_{10}H_{15} \\ OC_2H_5 \end{array} + \begin{array}{c} H \\ H \end{array} >C \begin{array}{c} \\ \\ OC \end{array} > C_8H_{14} \rightarrow C_8H_{14} \begin{array}{c} C:CHONa \\ \| \quad H \\ CO \end{array} +$$

$$C_{10}H_{16}O + C_2H_5OH.$$

He explains similarly the acetoacetic ester synthesis, which is a special case of the Claisen condensation:

[1] Prac. Meth. Org. Chem., 2nd Am. Ed., p. 155.
[2] Ann. Chem. (Liebig), **281**, 328.

$$CH_3COOC_2H_5 + NaOC_2H_5 \rightarrow$$

$$CH_3C\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{-OC_2H_5}} + H_3CCOOC_2H_5 \rightarrow$$

$$CH_3C(ONa):CHCOOC_2H_5 + 2C_2H_5OH.$$
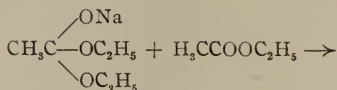
As seen from the above reactions, sodium ethylate is the active condensing agent. In the case of the acetoacetic ester synthesis a trace of alcohol is regarded as necessary to start the reaction. This reaction is cumulative because an increased amount of alcohol is being formed, and this, being acted upon by the sodium, gives an increasing amount of the active condensing agent—sodium ethylate. However, Claisen himself finds that sodium is a better condensing agent than sodium ethylate in alcoholic solution or sodium ethylate free from alcohol.

The explanation of the acetoacetic ester synthesis now advanced by Nef[1] is very similar to that of Claisen. The alcohol present in the ester forms sodium ethylate, and this reacts with ethyl acetate to form the intermediate compound

of Claisen, $H_3CC\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{-OC_2H_5}}.$ This substance is then supposed

to dissociate, giving $CH_2C\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{\big\langle}} + C_2H_5OH.$
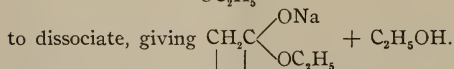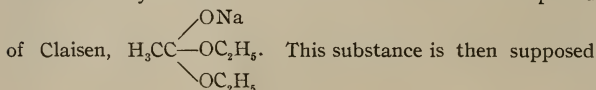
Another molecule of ester is assumed now to be added:

$$\underset{\displaystyle H\ \ CH_2COOC_2H_5}{CH_2C}\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{\big\langle}} \rightarrow CH_3C(ONa):CHCOOC_2H_5 + C_2H_5OH.$$
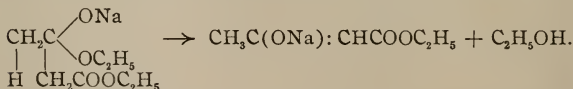
Higley[2] suggests that when ethyl acetate is treated with sodium two independent reactions take place simultaneously:

$$\text{I.} \quad 2CH_3COOC_2H_5 + 4Na \rightarrow \underset{\displaystyle CH_3CONa}{\overset{\displaystyle CH_3CONa}{\|}} + 2NaOC_2H_5.$$
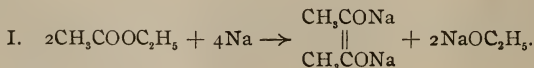
[1] Higley: This Journal, **37**, 293.
[2] *Ibid.*

II. The sodium ethylate formed in (I.) reacts on the ethyl acetate as follows:

II. $CH_3COOC_2H_5 + NaOC_2H_5 \longrightarrow$
$$CH_3C(ONa):CHCOOC_2H_5 + 2C_2H_5OH.$$
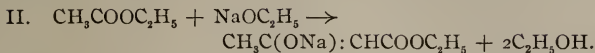
Here, again, it will be noted that sodium ethylate is the active condensing agent.

Higley concludes that this synthesis ought to give the best results when sodium ethylate is used as the condensing agent, as the reaction would then proceed entirely in the direction of the formation of acetoacetic ester until the point of equilibrium is reached, the reaction being a reversible one. This, he states, is reached when about 36.5 per cent of the acetoacetic ester has been formed. As found experimentally, however, the yield of the ester is not improved by the use of sodium ethylate, and, on the other hand, it is probable that sodium wire is the better condensing agent. This fact has been recorded by Claisen[1] and others, and the experiments herein described lead to the same conclusion.

Unless the superiority of sodium ethylate can be proved, the explanation of Higley is certainly not a logical one. Taking into consideration the present evidence as to the yield obtained in this synthesis when sodium and sodium ethylate are employed, if his explanation were correct, we should have the phenomenon of a condensing agent, formed at the expense of some of the ester used, proving more efficient than does the same agent when it is added to the original amount of the ester.

If the hypothesis of Claisen is correct, it is evident that sodium ethylate itself ought to be an excellent accelerator. This is found to be the case. In a series of experiments with camphor and the esters of various acids, using petroleum ether (b. p. 36°) as a solvent, the addition of a little alcoholic sodium ethylate accelerated a reaction to a marked degree. Absolute alcohol proved to be a still stronger accelerating agent. On the other hand, the use of sodium ethylate free from alcohol affected very little, if at all, the speed of the reaction.

[1] Ber. d. chem. Ges., **38,** 709.

The most striking fact brought out by these experiments is the *great reduction in the yield of the diketone, when alcohol or alcoholic sodium ethylate is added to the reacting materials.* In the condensation of ethyl phthalate and camphor, the addition of two drops of alcoholic sodium ethylate reduced the yield of diketone about 50 per cent. The addition of a little alcohol causes an equally great reduction. A similar reduction was observed in every case where either of these reagents was used. When alcohol is employed it undoubtedly attacks some of the sodium, but this in no way accounts for the great reduction in the yield of the product; the solution of sodium in alcohol which was employed in our experiments had been treated with sodium until no more would dissolve.

Sodium ethylate free from alcohol did not materially decrease the yield of the diketone, but it is not as good a condensing agent as sodium wire. Claisen,[1] in his paper on oxymethylenecamphor, states that alcoholic sodium ethylate is the weakest condensing agent, being followed in this respect by sodium ethylate free from alcohol and by sodium wire, in the order named. It has been experimentally established during this work that there is no difference in the solubility of sodium ethylate in ether, which was the solvent generally used by Claisen, and in the other solvents here employed. This is true of both the alcoholic solution of sodium ethylate and of that reagent free from alcohol.

Michael and others have pointed out that one of the weakest points in Claisen's explanation of the reaction which bears his name consists in the way in which he explains the influence exerted by sodium ethylate on the nature and extent of the changes involved. If sodium ethylate, or an analogous compound, is the active agent in promoting the condensation, then the addition of this compound should facilitate the reaction in question instead of retarding it. If the condensation is a reversible reaction this view would apply still more strongly. With regard to Claisen's claim that a trace of alcohol is necessary to start the reaction, we have already pointed out that two drops of alcoholic sodium ethylate reduces the yield by

[1] *Loc. cit.*

nearly one-half, and that alcohol has a similar effect. It is hard to understand how it can reasonably be claimed that a reaction depends on the presence of a hypothetical trace of alcohol, when, as a matter of fact, the yield is so greatly reduced by the presence of the smallest tangible amount of the substance. The attempted explanation by Claisen[1] and by Higley[2] of the superior condensing power of sodium is, to say the least, not satisfactory.

A number of experiments have been carried out with the following objects in view: (*a*) To determine the effect of varying the amount of sodium used in the condensation. (*b*) To find out at what point in the condensation the catalytic agent exerts its accelerating influence. (*c*) To determine whether there is a difference in the mechanism of this reaction when aromatic esters are used instead of those of the aliphatic group.

Bouveault and Locquin[3] showed that when sodium acts upon the aliphatic esters in the presence of a solvent the reaction proceeds as follows:

$$\begin{matrix} RCOOC_2H_5 \\ RCOOC_2H_5 \end{matrix} + 4Na \rightarrow \begin{matrix} RCONa \\ \| \\ CCONa \end{matrix} + 2NaOC_2H_5.$$
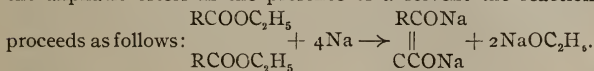
The experiments with ethyl oxalate, herein described, show that this similarly combines with four atoms of sodium to one molecule of the ester. In the case of ethyl malonate, only two atoms of sodium will react with each molecule of the ester, and the first atom of the metal causes a generation of hydrogen while the second does not. In view of the reactions of the other esters of the aliphatic group, it is difficult to reconcile this reaction with the formula usually assigned to ethyl malonate. On the other hand, it has been suggested by various chemists that in some reactions its behavior accords better with the formula $C_2H_5OC(OH):CHCOOC_2H_5$.[4] If this hypothesis is correct we should expect that the first atomic proportion of sodium would liberate hydrogen from the hydroxyl group, and that the resulting compound, $C_2H_5OC(ONa):CHCOOC_2H_5$, would form,

[1] Ber. d. chem. Ges., **38**, 712.
[2] *Loc. cit.*
[3] *Ibid.*
[4] Cf. D. Vorländer: Ber. d. chem. Ges., **36**, 268 (1903); E. Fischer and Dilthey: *Ibid.*, **35**, 844 (1902); Hans Meyer: *Ibid.*, **39**, 198 (1906).

with another portion of the metal, sodium ethylate and a sub-
stance having the constitution
$$\begin{array}{c} C_2H_5OC(ONa):CHCONa \\ \| \\ C_2H_5OC(ONa):CHCONa \end{array}$$
. In the
formation of camphoroxalic acid, J. Bishop Tingle[1] found that
the best yield resulted from the use of one atom of sodium and 1.5
molecules of camphor to one molecule of the ester, using ligroin
as a solvent. Wislicenus[2] has also studied the effect of an ex-
cess of sodium on ethyl acetate.

The experiments which have been performed in this investi-
gation have brought out the following facts: When the esters of
the aliphatic series are condensed with camphor, the use of
more than one atomic proportion of sodium does not increase
the yield of the diketone. The catalytic agent does not ac-
celerate the reaction between sodium and the ester, nor between
sodium and camphor. Sodium camphor is a weak condensing
agent. Only traces of the acid involved are found in the prod-
ucts of the condensation.

When ethyl benzoate and camphor are condensed, two atoms
of sodium combine with one molecule of the ester to give the
compound
$$\begin{array}{c} C_6H_5CONa \\ \| \\ C_6H_5CONa \end{array}$$
, which is the product obtained by Nef[3]
upon treating benzil with sodium, and is analogous to the com-
pound obtained by Bouveault and Locquin[4] with the aliphatic
esters. When this compound is treated with water, sodium
benzoate and benzyl alcohol are formed in equimolecular pro-
portions. Under suitable conditions, however, the hypothet-
ical product of hydrolysis,
$$\begin{array}{c} C_6H_5COH \\ \| \\ C_6H_5COH \end{array}$$
, changes into benzoin,
$C_6H_5CH(OH)COC_6H_5$; and this has been isolated in the form of its
m-nitrobenzene derivative. The best yield of diketone is ob-
tained when two atoms of sodium are allowed to react upon the
ester, and sodium camphor is then added. When camphor was
mixed with the reaction products of the ester with two atoms

[1] J. Chem. Soc., **57**, 652.
[2] Ann Chem. (Liebig), **186**, 163.
[3] *Ibid.*, **308**, 287.
[4] *Loc. cit.*

of sodium, the yield of the diketone was less than when the ester, camphor, and two atoms of sodium were allowed to react together.

The products obtained from the ethyl benzoate-camphor condensation are benzoic acid, benzyl alcohol, and the diketone. Apparently the formation of the diketone diminishes the amount of the benzyl alcohol obtained but does not effect the quantity of benzoic acid formed. It was found that only traces of benzoic acid are produced from the hydrolysis of ethyl benzoate during the process used for the extraction of the diketone, so that the presence of the acid in the condensation product cannot be accounted for in this way. In the condensation of ethyl cinnamate and camphor a large quantity of the acid is also obtained in the product. In the condensation of ethyl phthalate, however, only traces of the acid are found.

These results seem to show that the mechanism of the reaction is not always the same. Nevertheless, the relative strength of the condensing materials employed, the effect of catalytic agents, and the influence of sodium ethylate and alcohol seem to extend to the condensation of esters of both the aliphatic and aromatic series.

It has been pointed out that the experimental facts obtained in this investigation cannot be reconciled with the theories of Claisen, Nef, and Higley concerning the mechanism of the reaction. An alternative theory, which was advanced by A. Michael,[1] may be expressed as follows: Sodium at first acts upon one molecule of ethyl acetate, displacing hydrogen,

$$CH_3COOC_2H_5 + Na \longrightarrow CH_2NaCOOC_2H_5 + H.$$

This substance then reacts upon a second molecule of the ester, giving the product $CH_3C \overset{\displaystyle ONa}{\underset{\displaystyle CH_2COOC_2H_5}{\diagup}} OC_2H_5$. Alcohol is now eliminated with formation of the product $CH_3C(ONa):$ $CHCOOC_2H_5$. When sodium ethylate is used as a condensing agent, it is assumed that it causes, by the loss of some of its energy, an aldol condensation, forming, for example,

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[1] Ber. d. chem. Ges., **33**, 3731; **38**, 1934.

the product CH_3C
$\diagdown$
$\begin{array}{c}\diagup OH\\ -OC_2H_5\\ \diagdown CH_2COOC_2H_5\end{array}$
. This then yields the ortho

sodium derivatives formulated above, and finally, by the loss of alcohol, ethyl sodioacetoacetate. Michael, later, adopted the view that the compound formed when sodium acts on ethyl acetate is $CH_2:C(ONa)OC_2H_5$ instead of $CH_2NaCOOC_2H_5$. In view of recent work on tautomerism it seems likely that these two forms are in equilibrium.

The most striking differences between the two hypotheses appear to be the following: (1) Claisen assumes that it is not sodium itself which is the active agent, but a compound of the metal, such as sodium ethylate or sodium camphor; (2) The intermediate ortho compound is supposed by him to be an O- and not a C-derivative.

The reversal of the ethyl acetoacetate condensation, under the influence of sodium ethylate, has been studied very successfully by W. Dieckmann.[1] He shows that the velocity of the decomposition depends upon the degree of acidity of the particular β-ketonic ester employed. In conjunction with A. Kron,[2] in a paper which appeared while this article was in the press, he has also proved that the condensation may take place between esters and ketones of the type HCR_2CO. This fact is accounted for without difficulty by Michael's explanation of the acetoacetic ester condensation, but is incompatible with Claisen's theory. According to the latter the formation of the hypothetical intermediate compounds requires two atoms of hydrogen from the ketone, consequently the condensation can occur only between esters and ketones which contain the group H_3CCO or H_2CRCO.

With two reservations, noted below, the explanation of the mechanism of the condensation offered by Michael seems to be entirely satisfactory. The first reservation concerns the reaction of sodium on esters. Bouveault and his colleagues have proved how generally this reaction applies to compounds of the aliphatic series with the exception of ethyl acetate, which, as

[1] Ber. d. chem. Ges., **33**, 2670 (1900).
[2] *Ibid.*, **41**, 1260 (1908).

they have noted, acts in a different manner. It has been shown in the preceding pages that the reaction is the chief one which occurs with sodium and ethyl benzoate, in the presence of camphor; indeed, there can be no doubt that this, and not the Claisen condensation, is the preponderating reaction under the conditions described. It occurs, probably, in all cases where esters and sodium are brought together, its extent being determined by the nature of the ester and the experimental conditions. Obviously, these remarks, which are merely made for completeness, in no way modify Michael's explanation of the Claisen reaction itself.

The second point to which attention must be called is the catalytic effect of ether and the tertiary bases. In considering this the following facts must be remembered: (1) The substances in question accelerate the Claisen condensation; (2) they act in the same manner in connection with the formation of the Grignard reagent (Grignard, Tschelinzeff); (3) ether facilitates the addition of ethyl iodide to triethylamine (Menschutkin); ether is markedly active in promoting the action of sodium on acetone (Freer); ether, as compared with petroleum ether, facilitates the action of sodium on ethyl acetate; ether is without effect on the interaction of sodium and ethyl benzoate.

The explanation already offered of the effect of ether and the tertiary bases on the formation of the Grignard reagent can be applied, *mutatis mutandis*, to cover, in a satisfactory manner, the points mentioned above. It postulates the formation of an oxonium compound, which, in the case of acetone, for example,

would be $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O < \begin{matrix} H \\ OC < \begin{matrix} CH_3 \\ CH_2 \end{matrix} \end{matrix}$, whereas, with a ketone such as

camphor the formula $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O < \begin{matrix} H \ CH \\ \| \\ O.C \end{matrix} > C_8H_{14}$ would apply. The

next step in the condensation of camphor with an ester, such as ethyl oxalate, for instance, would be, adopting Michael's formulation, the production of the compound

$$C_6H_{14} \Big\langle \begin{array}{l} CHC(OH)(OC_2H_5)COOC_2H_5 \\ | \\ CO \end{array} ,$$
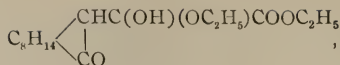
followed by that of the sodium derivative,

$$C_8H_{14} \Big\langle \begin{array}{l} CHC(ONa)(OC_2H_5)COOC_2H_5 \\ | \\ CO \end{array} ,$$
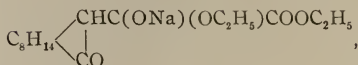
which then, by the elimination of alcohol, gives ethyl sodio-camphoroxalate, $C_8H_{14} \Big\langle \begin{array}{l} C:C(ONa)COOC_2H_5 \\ | \\ CO \end{array}$.
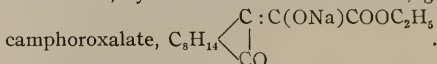
The above oxonium derivatives might also be expected to be more reactive with sodium than compounds having the ordinary ketone structure. The essential point in the explanation which is offered is that it represents a change into a secondary form of the ketone.

<center>EXPERIMENTAL.</center>

Method of Experimentation.—Unless otherwise stated, the ketone and ester were dissolved in the solvent employed and the sodium was cut under another portion of the solvent and quickly transferred to the press. The wire was now rapidly forced into the flask containing the solution, the flask being then attached to a reversed condenser.

The product of the reaction was poured into ice water, the mixture well shaken, and the lighter layer removed and dried over calcium chloride. Then the solvent was distilled away. The material remaining after the distillation will be referred to in the following pages as the "solvent product." The aqueous solution obtained after the separation of the solvent was, in some cases, extracted with ether; but except in a few special instances this treatment was found to be without appreciable effect, and the practice was discontinued. The aqueous solution was next acidified and extracted four times with ether. The ethereal solution, after being dried over calcium chloride, was distilled. The residue which had been dissolved in the ethereal solution will be referred to as the "acidification product."

For the acidification, acetic, dilute hydrochloric, or dilute sulphuric acid was employed. Carbon dioxide was also used. No difference in the effect of these substances has been discovered, and consequently, in the later stages of the work, dilute hydrochloric acid was used. A number of chemists have employed acetic acid for the preparation of such compounds as we have investigated; the mineral acid is far more convenient, and contamination of the "acidification product" with the excess of acetic acid extracted by the ether is avoided.

During the removal of the organic solvents by distillation the temperature was never allowed to rise above 100°, and was usually below this point. If necessary, the pressure was reduced.

A portion of the product of the reaction was dissolved in a few drops of ordinary alcohol (95 per cent). If alkali was present, the liquid was made faintly acid with pure, dilute hydrochloric acid. A few drops of an alcoholic solution of ferric chloride were added. The production of a reddish purple coloration was accepted as evidence of the formation of the enolic modification of the diketone.

The yields are sometimes referred to as "fair," "good," "poor," etc. It is a matter of regret that it has not been possible to be more definite on this point. Of course, the crude products of the reaction could have been weighed, and, in some cases, they were; but the figures obtained in this way would have been but little more definite and would probably have proved somewhat misleading. Reliable results can only be obtained by working out a method of purification for each individual compound, and it was impossible to attempt this because of the time required. The object has been to obtain general information and data, which could be used in a closer and more intensive study of these separate substances individually.

Preparation of Solvents and Reagents.—The solvents which have been employed were dried by means of sodium wire. When this was no longer tarnished, the liquid was decanted or filtered into a separate vessel, and a fresh portion of sodium wire was added. The solvent was allowed to remain in contact with this until used.

The esters were generally distilled, or their boiling points or melting points taken. Any free acid or acid ester was removed by washing with aqueous sodium hydroxide, and the compound was then dried by prolonged contact with calcium chloride.

The sodamide which was employed was made by the admirable method described by Winter,[1] which he worked out under the direction of Prof. Renouf.

The metallic calcium was the commercial article, prepared electrolytically. This was turned to thin shavings on a lathe, the outer portion covered with oxide being discarded. The shavings were washed in dry ether, rapidly dried in warm air, and placed in a warm, dry bottle which was then sealed with paraffin. Under these conditions it remained bright for an indefinite time. The statement has been made[2] that the oxide adhering to the original sticks of the metal can be removed by immersion for a short time in 70 per cent alcohol. This plan was tried but the results were not encouraging.

The solution of sodium ethylate in alcohol was made by adding clean, bright sodium to absolute alcohol, suitably protected from moisture, until no more would dissolve.

Sodium ethylate free from alcohol was prepared by dissolving the sodium in a mixture of absolute alcohol and petroleum ether, the liquid being finally boiled for two hours to complete the reaction. It was now distilled until the contents of the flask were dry. The residue was quickly powdered and sifted, and used for further reactions as soon as possible after it was prepared.

The absolute alcohol was obtained by treating ordinary alcohol first with quicklime, then with dehydrated copper sulphate, and finally boiling it for several days with calcium turnings, from which it was eventually distilled. It was well protected from moisture and was used soon after its preparation.

The apparatus in which the condensation was carried out was carefully washed with alcohol and ether and dried by a current of hot air. During the whole course of the experiment the vessels in use were protected from moisture by means of

[1] J. Am. Chem. Soc., **26**, 1484 (1904).
[2] Ber. d. chem. Ges., **38**, 3613 (1905).

calcium chloride tubes. Comparative experiments show that with some substances, at any rate, this latter precaution is unnecessary. It was adopted, however, in the case of all experiments which are described, unless otherwise stated expressly. It seems certain that the presence of traces of moisture is practically without effect on the condensation of some substances.

The sodium wire was obtained by placing clean, bright sodium in a sodium press and forcing it directly into the flask and solvent to be used for the condensation.

For the sake of brevity the work described in the following pages is given as if it were the result of single experiments. Actually, however, each experiment has been performed twice, and in many cases three or more times, until the evidence concerning the constancy and correctness of the observations made was satisfactory. Numerous changes were made in what may be termed the minor experimental conditions, but it has not been considered necessary to record these unless their results established some point which seems to be of importance.

Experiments Showing the Effect of Different Condensing Agents.

A. Experiments with Calcium Turnings.

Experiment 1.—22.8 grams camphor (1.5 mols.); 14.6 grams ethyl oxalate (1 mol.); 4.0 grams calcium (1 mol.); 400 cc. hexane (b. p. 90°).

After boiling for 40 minutes no signs of a reaction were observed. The addition of 25 cc. of absolute alcohol produced no effect. The solvent was distilled off and the condensation commenced immediately; after heating on a boiling water bath for one hour the calcium all disappeared. Two hundred cc. of petroleum ether were added and the product was extracted as usual. From the "acidification product" 10 grams of camphoroxalic acid were obtained.

Experiment 2.—The same as Exp. 1, except that 50 cc. xylene were used as the solvent.

No action resulted from heating for three hours. The solvent was distilled off and the residue again heated for two hours at 200° without result. Upon adding 50 cc. absolute alcohol and

heating at 100° for two hours the calcium was entirely dissolved. The product was extracted as in Exp. 1 and 10 grams of camphoroxalic acid were obtained.

Experiment 3.—The same as Exp. 1, except that 200 cc. of ether were used as the solvent.

No action took place during three hours at 36°. The addition of 75 cc. of pyridine produced no result.

Experiment 4.—22.8 grams camphor (1.5 mols.); 16.5 grams ethyl cinnamate (1 mol.); 4.0 grams calcium (1 mol.).

Boiling for two hours in 200 cc. hexane (b. p. 90°) produced no result. Fifty cc. of xylene were substituted for the hexane and the solution boiled for 4 hours without effect. When boiled for 4 hours at 160° without a solvent a reaction took place and part of the calcium was acted upon. The "acidification product" was a brown, semisolid mass. It was dissolved in ether and the solution extracted successively with aqueous solutions of sodium bicarbonate and sodium carbonate, cinnamic acid being thus removed. From the ethereal solution 5 cc. of a reddish brown oil were obtained which did not change after long standing. This gave a decided test with ferric chloride.

The "solvent products" obtained in the above experiment gave no tests with ferric chloride.

B. Experiments with Sodamide.

Experiment 5.—15.2 grams camphor (1 mol.); 14.6 grams ethyl oxalate (1 mol.); 3.9 grams sodamide (1 mol.).

No reaction resulted when hexane or xylene was used as solvents even when absolute alcohol was added. Upon heating for two hours without a solvent, at 150°, a reaction took place, a reddish brown mass resulting. From the "solvent" and "acidification products" were obtained 3 grams and 1 gram, respectively, of camphoroxalic acid.

Experiment 6.—The same as Exp. 5, using 200 cc. of ether and 75 cc. of pyridine as a solvent.

Boiling for 4 hours and standing at room temperature for some weeks produced no effect.

Experiment 7.—22.8 grams camphor (1.5 mols.); 15.0 grams ethyl benzoate (1 mol.); 3.9 grams sodamide (1 mol.); no solvent.

No reaction took place until the temperature was raised to 200°. The sodamide then disappeared within 5 minutes, and 5 cc. of a reddish brown oil giving a color test with ferric chloride were obtained. This gradually deposited benzoic acid. The residue consisted chiefly of ethyl benzoate. A small amount distilled at 230° to 245°. Very little condensation took place.

These experiments show that sodamide and calcium are far inferior to sodium unless the condensation takes place at a high temperature, at which the products must also be stable in order to obtain good yields.

EXPERIMENTS SHOWING THE EFFECT OF VARIOUS SOLVENTS AND TEMPERATURES.

A large number of condensations were carried out using as solvents varying quantities of ether, petroleum ether (b. p. 36°), ligroin (b. p. 50° to 55°), ligroin (b. p. 70° to 75°), hexane (b. p. 90°), benzene, toluene, and xylene. The esters used were ethyl formate, acetate, oxalate, benzoate, cinnamate, and phthalate. The products seemed equally soluble in all of the solvents and the solvent employed did not affect the yield of diketone obtained to any marked degree. The speed of the reaction seemed to increase with the temperature, except when ether was used as a solvent. In this case the reaction was accelerated to a marked degree, independently of the temperature.

EXPERIMENTS SHOWING THE EFFECT OF THE ESTERS OF VARIOUS ACIDS UPON THE CONDENSATION.

A. Aliphatic.

1. Esters of Monobasic Acids.

Experiment 9.—22.8 grams camphor (1.5 mols.); 7.4 grams ethyl formate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 300 cc. toluene.

After standing for a week at the room temperature, some of the metal remained unattacked. Consequently, the liquid was boiled for several hours. The yield of hydroxymethylene-camphor was fair.

Claisen's experiments on the preparation of hydroxymethyl-enecamphor were made with ether as a solvent.

Experiment 10.—22.8 grams camphor (1.5 mols.); 8.8 grams

ethyl acetate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 200 cc. ether.

The reaction commenced at room temperature, and at the end of twenty-four hours the liquid was dark brown, with a brown precipitate at the bottom. There was also a dark brown solid having the general form of the wire, but examination showed that it contained very little sodium. The flask, with its contents, was allowed to remain eight days longer at the ordinary temperature, but no further change could be detected at the end of that time. The "solvent product" consisted of a yellow liquid which gave no coloration with ferric chloride. From this some camphor crystallized. The "acidification product" was a reddish brown oil, which did not solidify when placed in a freezing mixture, nor by long standing. It gave a deep color with ferric chloride. Treatment of its ethereal solution with aqueous solutions of sodium bicarbonate, sodium carbonate, and potassium hydroxide, in the order named, failed to remove any compounds. The exact details of this attempted method of separation are described under Experiment 14.

Experiment 11.—22.8 grams camphor (1.5 mols.); 11.6 grams ethyl butyrate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 200 cc. ether.

The action commenced at once at room temperature, and appeared to be complete at the end of about twelve hours. The solution was reddish brown in color, with a dark brown precipitate, partly in the form of pieces of the wire. The "solvent product," which gave no coloration with ferric chloride, deposited unchanged camphor. The "acidification product" consisted of a reddish brown oil, which gave a deep color with ferric chloride and did not solidify. Treatment with alkali and alkaline carbonates, in the manner described under Exp. 14, failed to yield any tangible products.

2. *Esters of Dibasic Acids.*

Work with the ethyl oxalate compound is described under Experiments 1 to 6. In addition, an exhaustive study of its action on camphor has been made by J. Bishop Tingle,[1] who has also in-

[1] This Journal, **19**, 373 (1897); **20**, 318 (1898).

vestigated the behavior of the methyl, propyl, and isoamyl esters of the same acid.

Experiment 12.—22.8 grams camphor (1.5 mols.); 16.0 grams ethyl malonate (1.0 mol.); 4.6 grams sodium wire (1.0 atom); 300 cc. hexane (b. p. 90°).

A brisk evolution of hydrogen accompanied the action of the sodium upon the ester in the hexane. It commenced immediately after the introduction of the wire into the solution. A white, flocculent material soon covered the metal, and the liquid became distinctly pink. The evolution of gas ceased after twenty minutes. The product was boiled for fifteen minutes longer, which caused the disintegration of the wire and its ultimate solution. The camphor, dissolved in a small quantity of hexane, was now added, whereupon the liquid began to turn brown. After two hours' boiling the precipitate had completely disappeared and the liquid was of a deep reddish brown color. It was allowed to remain overnight at the ordinary temperature.

The "solvent product" consisted of a black liquid, containing camphor; it gave no coloration with ferric chloride. The "acidification product," which was a heavy, reddish brown oil, gave a deep coloration with ferric chloride. The yield of oil was about 2 cc.

Experiment 13.—22.8 grams camphor (1.5 mols.); 17.4 grams ethyl succinate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 250 cc. ether.

After an hour at the room temperature, the substances showed no signs of reacting; but, on boiling, the liquid became yellow and a yellow incrustation formed over the wire. At the end of eight hours' boiling the metal began to disintegrate. Heating was now stopped and the material allowed to remain at the room temperature for forty-eight hours. The "solvent product" was a red liquid, which gave a coloration with ferric chloride and deposited camphor. The "acidification product" consisted of a reddish brown oil, which formed a deep colored solution with ferric chloride.

B. Aromatic.

1. Esters of Monobasic Acids.

Experiment 14.—22.8 grams camphor (1.5 mols.); 15.0 grams

ethyl benzoate (1.0 mol.); 2.0 grams sodium wire (1.0 atom); 100 cc. hexane (b. p. 90°).

After two hours' heating on the water bath, the contents of the flask gradually became reddish brown. The material was allowed to remain overnight at the ordinary temperature. The "solvent product" consisted of a yellow oil, which did not solidify and gave no test with ferric chloride. The "acidification product" was a reddish brown oil, which formed a deep color with ferric chloride. After some days most of the compound had solidified. It was dissolved in ether and the solution well shaken with aqueous solutions of sodium bicarbonate, sodium carbonate, and potassium hydroxide, successively. The residue from the ethereal solution was dried, the ether distilled off, and the resulting reddish brown oil, which gave no signs of solidification when kept in a freezing mixture for several days, was treated in the manner described below.

The three alkaline solutions were acidified and extracted separately with ether, which was then dried and distilled. In this manner there was obtained from the sodium bicarbonate solution a relatively large quantity of benzoic acid. The sodium carbonate solution was found to have extracted benzoic acid, together with a little yellow oil. A mere trace of yellow solid was extracted from the potassium hydroxide solution. None of these substances gave any red coloration with ferric chloride.

Returning now to the purified reaction product, which gave a deep coloration with ferric chloride and weighed 3.5 grams; it was mixed with water (50 cc.), and 10 cc. aqueous sodium hydroxide solution (sp. gr. 1.15) was added. After remaining at the room temperature for forty-eight hours, the solution was red, and a reddish brown, sticky substance had deposited. The liquid was poured off, acidified with dilute sulphuric acid, and allowed to stand overnight. In this manner a small quantity of crystals was obtained; extraction of the acid liquor did not materially increase the yield of these. A small additional quantity of the compound was obtained by a second treatment of the yellow, resinous material with aqueous alkali hydroxide. The solubility of the compound did not lend itself to its ready purification. After many trials it was found that the best results

were obtained by the use of a mixture of acetone and water. In this manner, yellow, needle-shaped crystals melting at 91.5° were obtained. It gives a deep red color with ferric chloride. Analysis showed that the compound was not quite pure.

	Calculated for $C_8H_{14}\begin{cases} C:C(OH)C_6H_5 \\ | \\ CO \end{cases}$.	Found.
C	79.69	81.04
H	7.81	8.14

The investigation of this substance will be continued.

A number of attempts were made to obtain compounds of camphor with the ethyl nitrobenzoates. Sodium wire, alcoholic sodium ethylate, and sodium ethylate free from alcohol were employed as the condensing agents, and the temperature conditions were varied. It was found, in each case, that the last two condensing agents attacked the nitro group more or less vigorously, depending on the temperature. With sodium wire black compounds were formed. Apparently the hydrogen eliminated by the camphor reduced the nitro group to some extent, and the resulting products oxidized more or less on exposure to air.

Experiment 15.—22.8 grams camphor (1.5 mols.); 16.5 grams ethyl cinnamate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 500 cc. ether.

After the mixture had remained during ten minutes at the ordinary temperature the reaction had become very vigorous, and in the course of five minutes more, the sodium had dissolved completely. The liquid was a deep brown and a yellow, solid precipitate had formed; it was allowed to remain during twelve hours at the ordinary temperature.

The "solvent product" consisted of a reddish brown oil, which gave a decided coloration with ferric chloride. Before acidifying, the aqueous solution was again extracted with ether, to free it from traces of borneol and camphor, and the ether remaining in the aqueous solution was removed by a current of air. Acidification with acetic acid produced a milky precipitate, which, after twenty-four hours, had gathered on the dish in the form of a yellow, sticky mass that could not be filtered. The

mother liquor was decanted and the material dried. It gave a deep coloration with ferric chloride.

2. *Esters of Dibasic Acids.*

Experiment 16.—22.8 grams camphor (1.5 mols.); 22.2 grams ethyl phthalate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 300 cc. ether.

Immediately after mixing the materials the wire turned dark, and in the course of a few minutes the reaction was so violent that it was necessary to moderate it by immersing the flask in ice water. The wire had completely dissolved at the end of fifteen minutes, the solution assuming a golden brown color. It was allowed to stand overnight at the room temperature.

The liquid was poured into ice water, the mixture well shaken, and the ether removed. After evaporation it left a red liquid which gave a slight coloration with ferric chloride. The aqueous solution was extracted twice with fresh portions of ether and it was then treated with a current of air, until it no longer gave an odor of ether. Dilute acetic acid (1:1) was now added in excess. A yellow, sticky substance separated immediately; it was allowed to remain in contact with the mother liquor for twenty-four hours and was then filtered. After being dried it formed a yellow resin, was readily soluble in alcohol, and gave a deep coloration with ferric chloride. The acid mother liquor was extracted with ether. This extract left a quantity of reddish brown oil which gave an intense coloration with ferric chloride. This oil, in the course of a week, changed almost completely into a white solid which gave no coloration with ferric chloride. The resinous material spoken of above also changes slowly into a white solid giving no reaction with ferric chloride. It appears as if there were here an unstable enolic and a stable ketonic form of the diketone, which produce an equilibrium mixture after the liberation of the former. The supposed ketonic form is insoluble in alcohol, ether, and benzene. The supposed enolic form is soluble in all of these. If the enolic form is dissolved away from an equilibrium mixture of the two forms, it will slowly commence to deposit more of the supposed ketonic form.

This substance is now under investigation.

INFLUENCE OF CATALYTIC AGENTS ON THE CLAISEN CONDENSATION.

Experiment 17.—22.8 grams camphor (1.5 mols.); 15.0 grams ethyl benzoate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 400 cc. petroleum ether (b. p. 36°).

An action commenced slowly at the room temperature. The wire continued bright or white for two hours, during which time a yellow precipitate deposited in the flask. The liquid now became yellow and gradually darkened, finally becoming deep red. The wire also darkened and acquired a reddish brown coating, but five days were required before it disappeared. The solution and precipitate were treated separately with water, acid, etc. About equal amounts of the ''acidification products'' of the solution and the precipitate were obtained. They consisted chiefly of benzoic acid, together with a reddish brown oil which gave a coloration with ferric chloride. The ''solvent product'' was a yellow oil which gave a coloration with ferric chloride. The yield of diketone was poor, about 4.0 grams of the crude diketone and 2.3 grams of benzoic acid being formed.

Experiment 18.—Same as Exp. 17. Added as a catalytic agent 100 cc. ether.

A reaction commenced at once, and after about an hour the solution had about the same color as described in Exp. 25, but the precipitate was not quite as heavy and the coating on the wire was much thicker. At the end of two hours all but a slender thread of sodium had disappeared; the liquid was deep red and the precipitate a very deep brown. It was allowed to remain overnight. The yield of diketone was about the same as that obtained in Exp. 17.

Experiment 19.—Same as Exp. 17. Added as a catalytic agent 75 cc. pyridine.

The liquid quickly assumed a bluish tinge, the wire acquired a dark coating, and there was a small quantity of a white, flocculent precipitate. At the end of two hours this precipitate had disappeared, but another one, almost black, had collected at the bottom of the flask. The liquid was reddish brown, and the metal had almost all reacted. The mixture was allowed to remain overnight. The yield was practically the same as in the

preceding experiments and the velocity of the reaction essentially equal to that produced by ether.

Experiment 20.—Same as Exp. 17. Added as a catalytic agent 10 cc. quinoline.

The reaction commenced at once. The liquid and wire both darkened and the metal became covered with a rough coating, a brown precipitate being also deposited on the bottom of the flask. The liquid was boiled during two hours, at the end of which time most of the metal had reacted. The product was allowed to remain overnight. The yield was practically identical with that obtained in the previous experiments.

Experiment 21.—22.8 grams camphor (1.5 mols.); 16.5 grams ethyl cinnamate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 500 cc. ether.

After remaining for ten minutes at the ordinary temperature the reaction had become quite brisk, and at the end of five minutes more the sodium had disappeared. The liquid was deep brown with a yellow solid which did not adhere to the metal. The "solvent product" consisted of a yellow oil. The "acidification product" was, at first, entirely liquid, but gradually deposited a red, sticky solid which was removed. All three products gave deep colors with ferric chloride.

Experiment 22.—The same quantities of camphor, ester, and sodium as in Exp. 29; 300 cc. petroleum ether (b. p. 36°).

Hardly any action had taken place at the end of two hours, consequently, 25 cc. of ether were added. This caused the rapid production of a red solid, the wire remaining bright throughout the experiment. At the end of two hours most of the metal had dissolved and the remainder disappeared after the mixture had been allowed to stand overnight. The yield was practically the same as in the preceding experiment.

Experiment 23.—22.8 grams camphor (1.5 mols.); 22.2 grams ethyl phthalate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); 400 cc. petroleum ether (b. p. 36°).

During six hours at room temperature, the wire gradually darkened and assumed a brown coating, which then slowly deposited at the bottom of the flask. The liquid became yellow. After remaining overnight practically all the sodium had re-

acted, but much of the solid product retained the original form of the wire coils. The yield was as good as any which has been obtained.

Experiment 24.—Same as Exp. 23. Added as a catalytic agent 50 cc. ether.

The mixture without the ether was allowed to remain for an hour at room temperature. The ether was then added. The action immediately became more rapid, and at the end of three hours the metal had completely disappeared and a finely divided, dark brown precipitate had formed. This was allowed to remain during twenty-four hours at the room temperature. The yield of diketone was about equal to that previously obtained.

Experiment 25.—Same as Exp. 23. Added as a catalytic agent 10 cc. of quinoline.

In five minutes the wire became red, and at the end of three hours all of it except a thin thread had reacted. The liquid was reddish brown, and a black precipitate had formed. A good yield of the product was obtained, but it appeared to consist entirely of what is believed to be the ketonic form of the diketone. Although the reaction did not take place as rapidly as when ether was employed as the catalyst, there is no doubt as to the large accelerating influence of quinoline.

Experiment 26.—Same as Exp. 25, except that ethyl oxalate was used instead of ethyl phthalate.

The object of this experiment was to see if quinoline had any influence on the production of (enolic) camphoroxalic acid. The product, however, appeared to be identical with the ordinary form of the acid. In view of Michael's investigation of the action of tertiary bases and desmotropic compounds,[1] this result is what might be expected.

Experiment 27.—Same as Exp. 23. Added as a catalytic agent 100 cc. pyridine.

This experiment was performed to see if pyridine, as well as quinoline, tended to promote the formation of the supposed ketonic form.

At the ordinary temperature the wire and liquid immediately darkened, and a black precipitate formed. After an hour al-

[1] Ber. d. chem. Ges., **39,** 209 (1906).

most all the sodium had dissolved, and the following morning it had completely disappeared. Neither of the products of this reaction gave any coloration with ferric chloride. The catalytic influence of pyridine was plainly evident.

Investigation of Conditions Affecting the Formation of the Grignard Reagent.

The object of these experiments was to discover whether the Grignard reagent can be formed under certain conditions, at a relatively low temperature, in the absence of ether or a tertiary base. For this purpose it was, obviously, desirable to use a halogen derivative which possessed the maximum activity toward magnesium. Some of our experiments were made with ethyl chloracetate, which was found to be well adapted to our purpose.

Experiment 28.—12.0 grams ethyl chloracetate (2 mols.); 1.22 grams magnesium ribbon (1 atom); 50 cc. ether.

The reaction took place so rapidly that it was necessary to cool the materials in a freezing mixture.

Experiment 29.—This was the same as Exp. 28, except that 200 cc. petroleum ether (b. p. 36°), were used in place of the ether. No apparent action was observed after several hours' boiling, consequently a little iodine was added and the heating continued for ten hours longer. The liquid had turned yellow at the end of this time, and a yellow, crystalline precipitate coated the metal and settled to the bottom of the flask.

Experiment 30.—The conditions were the same as in Exp. 29, except that the solvent consisted of 35 cc. of ether in addition to the petroleum ether. After three hours' boiling a heavy precipitate had formed and at the end of ten hours this was largely augmented. Action was much more rapid than in the preceding experiment.

Experiment 31.—This was carried out exactly as in the case of Exp. 29, except that the solvent petroleum ether was reduced to 50 cc. Most of the magnesium had dissolved after boiling for sixteen hours. Evidently a greater concentration of the ester favors its attack on the metal.

Experiment 32.—7.80 grams ethyl iodide (1 mol.); 1.22 grams

magnesium ribbon (1 atom); 50 cc. petroleum ether (b. p. 36°); 30 cc. quinoline.

No reaction took place at the ordinary temperature, but after boiling for twenty minutes most of the metal had dissolved and a red mass formed. With benzoic aldehyde this substance gave a rather poor yield of the secondary alcohol.

Experiment 33.—This was similar to the preceding experiment, except that 25 cc. of ether were used instead of the quinoline, and the quantity of petroleum ether was reduced one half. The action commenced at the ordinary temperature, the liquid soon began to boil, and after half an hour most of the metal had dissolved. Treatment of the product with benzoic aldehyde gave an excellent yield of the secondary alcohol.

Experiment 34.—7.80 grams brombenzene (1 mol.); 1.22 grams magnesium ribbon (1 atom); 200 cc. petroleum ether (b. p. 36°); 5 cc. quinoline.

No apparent change took place after two hours boiling; consequently, a little iodine was added and the heating was continued during ten hours. A red compound was formed, which reacted only slowly with benzoic aldehyde, and the yield of secondary alcohol was poor.

Experiment 35.—This was a repetition of the preceding experiment, but 50 cc. of pyridine were used instead of the petroleum ether and quinoline. The results were similar to those recorded above, except that the metal had almost all disappeared after four hours' boiling.

Experiment 36.—A similar experiment to Exp. 34, except that the quantity of petroleum ether was reduced to 50 cc. and 15 cc. of pyridine were added as the catalytic agent. Most of the metal had dissolved after six hours' boiling. The product of the reaction was similar to those described above.

EFFECT OF SOLVENTS AND CATALYTIC AGENTS ON THE SYNTHESIS OF ETHYL ACETOACETATE.

Under ordinary conditions the synthesis of ethyl acetoacetate, as is well known, is carried out by the use of ethyl acetate in excess, the excess acting as the solvent. It was desired to ascertain the effect upon the reaction of the use of petroleum ether

as a solvent, and also to determine the action of catalytic agents such as ether and pyridine.

Experiment 37.—17.6 grams ethyl acetate (2 mol.); 2.3 grams sodium wire (1 atom); 50 cc. petroleum ether (b. p. 36°).

During the first half hour a slight reaction took place, some white, flocculent matter was formed and then disappeared, and there was a slight evolution of hydrogen. The liquid turned yellow gradually, but there was no further change during fourteen hours at the room temperature. After four days under the same conditions the liquid was darker. The wire retained its form, although most of the metal had reacted. The product of the reaction was treated in the manner described by Gattermann.[1] After purification a portion boiled at 175° to 177° and this gave an intense color with ferric chloride.

Experiment 38.—This was the same as the preceding experiment except that 75 cc. of ether were added. The reaction was much more rapid than before. The mixture was allowed to remain during twelve hours at the ordinary temperature, then boiled for four hours, at the end of which time all the sodium had reacted. After remaining overnight the ethyl acetoacetate was separated and identified as described above.

Experiment 39.—In this case 35 cc. of ether were employed; otherwise the conditions were the same as in Exp. 37. The reaction was more rapid and a considerable quantity of the metal was dissolved during the first hour. It was allowed to remain overnight and then boiled for four hours. The product gave the same tests as in the preceding cases.

Experiment 40.—This was also the same as Exp. 37, except that 35 cc. of pyridine were added. At the end of an hour, at the ordinary temperature, the liquid was red, with some dark colored material at the bottom. After remaining overnight it was heated for two hours, when the sodium had, apparently, all reacted. The product gave the tests previously noted.

Experiment 41.—17.6 grams ethyl acetate (2 mol.); 2.3 grams sodium wire (1 atom); 35 cc. pyridine.

A reaction commenced immediately, the wire gradually becoming red, then black and, after heating during two hours, the

[1] Organ. Prep., 2nd Am. Ed., p. 155.

sodium was completely changed. The product was freed from pyridine by washing with dilute (1 : 3) hydrochloric acid and subsequently distilled under reduced pressure. The purified material gave the tests for ethyl acetoacetate.

EFFECT ON THE CLAISEN CONDENSATION OF THE PRESENCE OF ALCOHOL OR OF SODIUM ALCOHOLATE.

A. Solubility of Alcoholic Sodium Ethylate and of Sodium Ethylate Free from Alcohol.

No statement has been found regarding the solubility of these substances and, consequently, some qualitative determinations have been made in order to be in a position to judge as to whether its behavior was due primarily to changes of solubility in the varying solvents employed.

The alcoholic sodium ethylate was mixed with an equal volume of each of the following substances: Dry ether free from alcohol, petroleum ether (b. p. 36°), ligroin (b. p. 80°), hexane (b. p. 90°), toluene. No precipitate formed after remaining for an hour nor on heating the liquids. In all cases the solutions remained homogeneous.

Sodium ethylate free from alcohol, in a finely powdered condition, was added, in small quantity, to separate portions of each of the following liquids: Dry ether free from alcohol, petroleum ether (b. p. 36°), ligroin (b. p. 80°), hexane (b. p. 90°), benzene, pyridine, quinoline. In no case did any appreciable quantity dissolve.

B. Experiments on the Synthesis of Ethyl Acetoacetate.

Experiment 42.—17.6 grams ethyl acetate (2 mol.); 2.0 grams sodium wire (1 atom); 50 cc. petroleum ether (b. p. 36°); 10 drops of alcoholic sodium ethylate.

An action commenced at once, the sodium turning white and the liquid darkening rapidly. After remaining for an hour at the ordinary temperature, the liquid was boiled for two hours, at the end of which time the sodium had disappeared. The product gave traces of ethyl acetoacetate, as shown by the boiling point test and the coloration with ferric chloride.

Experiment 43.—17.6 grams ethyl acetate (2 mol.); 6.8 grams sodium ethylate free from alcohol (1 mol.).

The ester was added to the sodium ethylate without removing the latter from the flask in which it had been prepared. When heated on a water bath the solid turned brown and dissolved gradually. After ten hours one half of the product was removed and tested for ethyl acetoacetate, which was found to be present only in traces. To the remaining portion of the product 50 cc. of ether were added and the heating continued for ten hours longer. There was no change in the appearance of the material, but it yielded 2.5 grams of a liquid which boiled at 175° to 177° and gave a deep coloration with ferric chloride. This yield is 27 per cent of the theoretical, whereas, by the ordinary method the yield is about 30 per cent. The increased yield in the second part of the experiment is attributed to the catalytic action of the ether and not to the extra heating.

C. *Experiments with Ethyl Benzoate.*

Experiment 44.—22.8 grams camphor (1.5 mols.); 15.0 grams ethyl benzoate (1.0 mol.); 2.3 grams sodium (1.0 atom); 200 cc. petroleum ether (b. p. 36°); 25 cc. alcoholic sodium ethylate.

The liquid darkened immediately, and after ten minutes began to boil. The action was complete after thirty minutes, the liquid being dark, with a reddish brown solid at the bottom of the flask. It was allowed to remain overnight. The "solvent product" was a yellow oil which gave no coloration with ferric chloride. The "acidification product" consisted chiefly of benzoic acid, together with a very little diketone. The acid was extracted by means of an aqueous solution of sodium bicarbonate.

Experiment 45.—15.0 grams camphor (1 mol.); 15.0 grams ethyl benzoate (1.0 mol.); 2.3 grams sodium wire (1.0 atom); absolute alcohol.

The metal was dissolved in four times the theoretical quantity of absolute alcohol. The camphor was dissolved in the ethyl benzoate. The solutions were mixed, but no visible reaction took place. Heating on a water bath caused the deposition of a white, solid cake, which was completely dissolved at the end of two hours, the solution becoming gradually dark. The "solvent product" was similar to that obtained in the pre-

ceding experiment. The "acidification product" consisted of a red oil which gave no characteristic coloration with ferric chloride. It proved to consist almost entirely of ethyl benzoate, together with traces of benzoic acid.

Experiment 46.—22.8 grams camphor (1 mol.); 15.0 grams ethyl benzoate (1 mol.); 2.3 grams sodium wire (1 atom); 6.9 grams dry sodium ethylate; 200 cc. petroleum ether (b. p. 36°).

After mixing the materials the liquid became slightly dark at the ordinary temperature, during the course of an hour. It was allowed to remain overnight without heating, and was then dark brown, with a heavy, yellow precipitate. Most of the sodium had disappeared. The contents of the flask were treated in the usual manner. The "solvent product" resembled that in the two preceding experiments. From the "acidification product" some benzoic acid separated, together with 1.2 grams of diketone.

Experiment 47.—This was the same as Exp. 44, except that 25 cc. of absolute alcohol were used in the place of the same volume of alcoholic sodium ethylate. The reaction commenced at once and the liquid began to boil violently at the end of three minutes, so that it was necessary to immerse the flask in ice water. The action appeared to be complete after fifteen minutes. The "solvent product" resembled that obtained in Exp. 44. The "acidification product" consisted chiefly of ethyl benzoate, together with a relatively large quantity of benzoic acid. The quantity of diketone formed was very small.

D. *Experiments with Ethyl Phthalate.*

Experiment 48.—22.8 grams camphor (1.5 mols.); 22.2 grams ethyl phthalate (1 mol.); 2.3 grams sodium wire (1 atom); 400 cc. petroleum ether (b. p. 36°); 25 cc. alcoholic sodium ethylate.

A reaction commenced immediately, the wire and the liquid both turning dark. After fifteen minutes at the room temperature about half of the wire had dissolved. Action appeared to be practically complete at the end of two hours. The liquid was dark red, most of the wire had disappeared, and the remainder had entirely disintegrated. The "solvent product" was a yellow oil. Both it and the "acidification product" gave

a red color with ferric chloride, but the yield of the "acidification product" was only about one half of that obtained, under similar conditions, by the use of ether or a tertiary base as a catalytic agent.

Experiment 49.—This was the same as Exp. 48, except that only two drops of alcoholic sodium ethylate were employed. About four hours were required to complete the reaction. The product and the yield were practically the same as in the preceding experiment.

Experiment 50.—This was the same as Exp. 48, except that the alcoholic sodium ethylate was replaced by an equal volume of absolute alcohol. The sodium wire remained light colored for two minutes and then commenced to darken rapidly; two minutes later it was brown and the liquid reddish in color, and there was a considerable evolution of gas or vapor from the neighborhood of the wire. Fifteen minutes after the experiment was commenced the metal had disappeared and the liquid had assumed a deep reddish tint. It was allowed to remain overnight at the ordinary temperature. The "solvent product" was a yellow oil, which gave no coloration with ferric chloride. The "acidification product" consisted of about 3 cc. of a reddish brown oil, giving a deep color with ferric chloride. The oil rapidly changed to a white solid. The yield of condensation product was much smaller than that obtained in Exp. 48, where alcoholic sodium ethylate was used.

These results show that although a reaction is rapidly brought about by the use of alcoholic sodium ethylate, and even more rapidly by the use of absolute alcohol, yet the yield of diketone is diminished in every case and relatively large quantities of benzoic acid are obtained. Apparently no phthalic acid is formed under similar conditions. It is hoped that more light on this interesting point will be gained in a subsequent investigation.

THE EFFECT OF VARYING QUANTITIES OF SODIUM ON THE YIELD OF DIKETONE.

These experiments were carried out in connection with the ones described in the following section. Those esters were se-

lected which had been found to react the most readily with sodium. Bishop Tingle has described some work regarding the effect produced on the yield of camphoroxalic acid by varying proportions of sodium, and J. Wislicenus[1] studied the action of sodium, in excess, on ethyl acetate.

Experiment 51.—7.9 grams camphor (1 mol.); 7.3 grams ethyl oxalate (1 mol.); 4.6 grams sodium wire (4 atoms); 250 cc. hexane (b. p. 90°).

The wire was added to the ester and the solvent, and the mixture heated for about fifteen hours. At the end of this time the metal had reacted. The liquid was reddish brown and a red precipitate had formed. The camphor, dissolved in the remaining hexane, was now poured in and the heating continued for four hours. Most of the solid dissolved. The "acidification product" gave 5.3 grams of camphoroxalic acid, or 43 per cent of the theoretical yield. This is only about half the average yield obtained when one atomic proportion of sodium is added.

Experiment 52.—7.6 grams camphor (1 mol.); 7.3 grams ethyl oxalate (1 mol.); 2.3 grams sodium wire (2 atoms); 250 cc. ether.

Only one half the above quantity of sodium was added at first to the ester and the solvent. The reaction proceeded as in Exp. 51. The ether did not appear to affect the speed of the reaction between sodium and the ester. After heating during two hours on a water bath the wire retained its shape; the liquid was yellow, and a precipitate of the same color had formed. The remaining sodium was now added together with the camphor, the solution having been cooled to the room temperature. At the end of three minutes the liquid boiled and in twenty minutes the action ceased, although much of the wire still held its shape. The product was boiled for twenty minutes more and allowed to remain at room temperature for twelve hours. This treatment produced no visible change. Before the addition of the product to water and acid, about a gram of unchanged sodium was removed. The yield of crude camphoroxalic acid was 5.5 grams, which is 58 per cent of the theoretical.

[1] Ann. Chem. (Liebig), **186**, 193 (1877).

Experiment 53.—7.6 grams camphor (1 mol.); 8.0 grams ethyl malonate (1 mol.); 2.3 grams sodium wire (2 atoms); 250 cc. hexane (b. p. 90°).

As soon as the evolution of hydrogen, caused by adding the sodium to the ester and solvent, had ceased, the mixture was heated on a water bath during four hours, and then allowed to remain overnight at the ordinary temperature. A white, flocculent compound was present in the liquid, but much of the wire was unchanged. The mixture was boiled on a sand bath during twenty hours, at the end of which time about one half of the wire was unchanged. The liquid was yellow and the precipitate brown. The camphor, dissolved in hexane, was now added and the heating continued for four hours. The product was allowed to stand overnight. Some of the sodium was still unchanged; the liquid was a deep reddish brown, with a dark precipitate present. The "acidification product" consisted of 3.8 grams of a reddish brown oil which gave an intense color with ferric chloride.

Experiment 54.—8.75 grams sodium camphor (1 mol.); 8.00 grams ethyl malonate (1 mol.); 2.30 grams sodium wire (2 atoms); 300 cc. petroleum ether (b. p. 36°); 50 cc. ether.

The ester, one half the sodium, and the petroleum ether were mixed and allowed to remain at the room temperature during twelve hours. The mixture was then boiled for two hours, when the metal was dissolved. The remaining sodium was now added and the boiling continued. A yellow solid formed gradually. More sodium was then put in, but as it remained unchanged it was removed later. The sodium camphor and ether were now added. After boiling for six hours the solid was a deep brown. It was allowed to remain overnight. The "acidification product" consisted of 2.4 grams of oil, which gave an intense coloration with ferric chloride.

Experiment 55.—22.8 grams camphor (1.5 mols.); 15.0 grams ethyl benzoate (1 mol.); 2.3 grams sodium wire (1 atom); 50 cc. hexane (b. p. 90°).

The camphor, sodium, and solvent were mixed and heated for an hour. The product was light yellow, but on adding the ester it rapidly became brown. It was heated for another

hour. The "acidification product" was a white solid (benzoic acid), with a little reddish brown oil. The yield of diketone was poor.

Experiment 56.—11.4 grams camphor (1.5 mols.); 7.5 grams ethyl benzoate (1 mol.); 2.3 grams sodium wire (2 atoms); 300 cc. ligroin (b. p. 70°); 50 cc. ether.

After remaining for three hours at the ordinary temperature the wire was dark brown; it was boiled during four hours and allowed to remain overnight. The liquid was yellow and a brownish yellow precipitate had formed. After being heated for two hours longer and allowed to remain at the ordinary temperature for twenty-four hours, the wire had almost completely changed and most of the product was in solution. The "acidification product" consisted of 5.3 grams of a yellow solid, from which 2 grams of benzoic acid were separated by means of an aqueous solution of sodium bicarbonate, after dissolving the product in ether. The residual diketone weighed 0.7 gram. The "solvent product" was distilled with steam. The volatile material consisted of 2.1 grams of benzyl alcohol and 6.0 grams of a mixture of camphor and borneol. The nonvolatile portion failed to react with phenylhydrazine or with *m*-nitrobenzoyl chloride and alkali.

Experiment 57.—This was a duplicate of the preceding experiment, except that twice as much sodium wire was employed. The reaction proceeded in the manner described. The "solvent product" yielded a little camphor and borneol, but only traces of benzyl alcohol. The "acidification product" consisted of 8.3 grams of solid, which gave 2.7 grams of benzoic acid and 2.2 grams of crude diketone.

Experiment 58.—The quantities of substances used were the same as in Exp. 57, but the two atomic proportions of sodium were allowed to react with the ester. After two hours' heating the liquid was yellow, with a red precipitate present; the wire was golden brown. The heating was continued for six hours longer, when the precipitate was light brown and the liquid yellow. Almost all of the sodium had reacted. The camphor was now added and the heating continued dur-

ing seven hours. The solvent was yellow and the precipitate a deep reddish brown. The "solvent product" gave 4.4 grams of camphor and borneol, and only traces of benzyl alcohol. The "acidification product" consisted of 12.8 grams of reddish brown oil, from which 3.8 grams of benzoic acid and 1.0 gram of crude diketone were separated.

Experiment 59.—7.6 grams camphor (1 mol.); 7.5 grams ethyl benzoate (1 mol.); 6.9 grams sodium wire (3 atoms); 300 cc. ligroin (b. p. 70°); 50 cc. ether.

The ester was treated with two thirds of the sodium and the camphor with the remainder. In neither case did the ether appear to exert a catalytic influence. When the products were mixed no change took place at the ordinary temperature. After heating during seven hours, the liquid was reddish brown, with a dark brown precipitate present. The "solvent product" was a yellow oil, consisting mainly of the higher-boiling solvent. Benzyl alcohol could not be detected. The "acidification product" consisted of 7.5 grams of a reddish brown oil, from which 3.0 grams of benzoic acid and 4.4 grams of the crude diketone were obtained.

ACTION OF SODIUM ON ETHYL BENZOATE.

Bouveault's interesting work on the interaction of sodium and the aliphatic esters has been referred to previously. The action of sodium on ethyl benzoate has been investigated by Claisen and others. The main object of these experiments was to try to gain additional knowledge regarding the nature and reaction of the products formed from the metal and ester.

Experiment 60.—13.7 grams ethyl benzoate (1 mol.); 2.1 grams sodium wire (1 atom); 19.85 grams absolute alcohol; 200 cc. petroleum ether (b. p. 36°).

An action commenced at once. Hydrogen was, of course, evolved and the solution darkened rapidly. At the end of an hour most of the metal had reacted; the solution was reddish brown and a light colored precipitate was present. The flask was allowed to remain at room temperature for two hours longer. The "solvent product" consisted of a yellow oil from which 9.7 grams of ethyl benzoate were obtained, but

no benzoic acid. The "acidification product" gave 2.6 grams of benzoic acid, equivalent to 2.3 grams of the ester. This leaves 0.9 gram of the ester unaccounted for.

Experiment 61.—15.0 grams ethyl benzoate (1 mol.); 4.6 grams sodium wire (2 atoms); 4.6 grams absolute alcohol (1 mol.); 2.3 grams sodium wire (1 mol.), to form sodium ethylate; 14.2 grams camphor (1 mol.); 200 cc. ligroin (b. p. 90°); 50 cc. ether.

The solvent and the alcohol were mixed and 4.6 grams of sodium wire (2.0 mols.) added. After heating for three hours reaction had ceased and a white precipitate had deposited in the bottom of the flask. The product was cooled to room temperature and the ethyl benzoate was poured in. The remaining wire gradually became yellow and then brown. At the end of an hour the solution was yellow and a heavy white precipitate was observed in the bottom of the flask. The coil of wire was brown. After boiling during two days the metal had all disappeared. A second atomic proportion of sodium was now added and the heating continued for two days longer. This caused almost all of the wire to react. A third atomic proportion of sodium was placed in the flask and the heating prolonged during several days, but no further appreciable reaction took place. The solution was now a reddish brown, with a bulky precipitate which, as seen through the solution, appeared to be yellow in color. The camphor, dissolved in some ligroin and ether, was now added to the product of the reaction and the heating continued for four hours. The "solvent product" was a yellow oil. The "acidification product" consisted of 5.6 grams of benzoic acid and 1.4 grams of crude diketone. The quantity of the acid is equal to 7.2 grams of the ester.

Experiment 62.—15.0 grams ethyl benzoate (1 mol.); 4.6 grams sodium wire (2 atoms); 200 cc. petroleum ether (b. p. 36°).

The ester, solvent, and half of the sodium were heated during eight hours, at the end of which time the metal had disappeared. The remainder of the sodium was then added, and the heating continued for ten hours longer. This portion of

the wire also dissolved, but there was no reaction when a third atomic proportion of the metal was added and the heating prolonged for another ten hours. The "solvent product" consisted of 0.7 gram of a yellow, amorphous solid. The "acidification product" contained 5.4 grams of benzoic acid, in addition to an amorphous substance from which no crystalline derivative could be obtained by the action of benzoyl chloride (cf. Exp. 66). Allowing for the unavoidable loss in the separation and purification, the above quantity of benzoic acid is equal to one-half of the ester used, the exact ratio being 6 grams of acid: 7.5 grams of ester.

Experiment 63.—7.5 grams ethyl benzoate (1 mol.); 2.3 grams sodium wire (2 atoms); 250 cc. ether.

The reaction commenced immediately and at the end of an hour a brown precipitate began to form. The heating was continued during three days, two additional atomic proportions of sodium being added, but these apparently not attacked. The "solvent product" consisted of 0.5 gram of a yellow oil, containing some white crystals. The "acidification product" yielded 3.9 grams of benzoic acid, equivalent to 5 grams of the acid. Speaking generally, this experiment presented the same features as those in which camphor and ethyl benzoate were condensed.

Experiment 64.—7.5 grams ethyl benzoate (1 mol.); sodium hydroxide (4 mols.); 250 cc. ether.

The hydroxide was equivalent to the total quantity of sodium used in the preceding experiment. It was dissolved in ice water and shaken with the ester, dissolved in the ether. The time occupied in the manipulation and the other conditions were exactly the same as those in Exp. 63. The "solvent product" consisted of 7.1 grams of ethyl benzoate, and the "acidification product," when dissolved in ether and treated with aqueous sodium bicarbonate, yielded 0.1 gram of benzoic acid, equivalent to 0.123 gram of the ester, thus leaving only 0.277 gram of the ester unaccounted for. This result shows that practically none of the benzoic acid which separated in the experiments described above can be formed as a result of the hydrolysis of ethyl benzoate during the extraction processes.

Experiment 65.—The "solvent products" from five different experiments with ethyl benzoate and camphor, under varied conditions, which had given very poor relative yields of diketone, were combined and distilled with steam. The volatile material was separated from the water, dried, and filtered. The solid consisted of 20 grams of a mixture of camphor and borneol. The liquid portion, after being fractionated, yielded 40 grams of benzyl alcohol, which is equivalent to about half of the ethyl benzoate employed.

Experiment 66.—3.75 grams ethyl benzoate (1 mol.); 1.15 grams sodium wire (2 atoms); 200 cc. ether.

The solid product of the reaction, which was carried out in the manner described under Exp. 63, was filtered quickly, washed several times with ether, in a closed flask, and the red solid obtained suspended in ether. Excess of *m*-nitrobenzoyl chloride and aqueous alkali were now added and the mixture shaken thoroughly. A compound deposited gradually as yellow crystals, which, after purification, melted above 310°. This substance was dissolved in 50 per cent alcohol, excess of aqueous sodium hydroxide added, and the liquid allowed to remain at the room temperature during two days. When acid was added to the solution a heavy, white precipitate was formed. This melted at 141° to 142° and was, therefore, identified as being *m*-nitrobenzoic acid. No benzoin was isolated, but the yellow compound of high melting point described above was prepared synthetically from *m*-nitrobenzoyl chloride and benzoin, in the presence of an alkali.

The results described above confirm the conclusion that, in addition to sodium ethylate, sodium and benzoic ester yield the compound $\begin{array}{c} C_6H_5CONa \\ \| \\ C_6H_5CONa \end{array}$, which, with water, gives sodium benzoate and benzyl alcohol, in equimolecular proportions. Under suitable conditions, however, the hypothetical hydrolysis product, $\begin{array}{c} C_6H_5COH \\ \| \\ C_6H_5COH \end{array}$, changes into benzoin, $C_6H_5CH(OH)COC_6H_5$, which was isolated in the form of its *m*-nitrobenzoyl compound.

The results also demonstrate that this reaction between the metal and the ester is by far the preponderant one under all the rather varied experimental conditions which have been employed.

The work described in the preceding pages was carried out at the University of Rochester, N. Y., and at the Johns Hopkins University. It will be continued by us during the coming academical year.

McMaster University,
Toronto, Canada,
July, 1907.

REACTIONS OF THE ARSINES.

By William M. Dehn.

In an earlier contribution[1] it was held that the reactions of the arsines and their derivatives can be divided into two general classes, *viz.*, those that involve

(1) Addition.

(2) Addition and subsequent dissociation; in other words, these reactions result from alternate changes of

(1) Trivalent arsenic to pentavalent arsenic, and

(2) Pentavalent arsenic to trivalent arsenic.

The oscillations of the arsenic valencies are best illustrated by the following reactions:

Halogen-Alkyl Series (A).

	(a)	(b)	(c)
I.	$AsX_3 + RX \longrightarrow$	$RAsX_4{}^2 \longrightarrow$	$RAsX_2 + X_2{}^3$
	$AsX_3 + RX \longleftarrow$	$RAsX_4{}^5 \longleftarrow$	$RAsX_2 + X_2{}^4$
II.	$RAsX_2 + RX \longrightarrow$	$R_2AsX_3{}^6 \longrightarrow$	$R_2AsX + X_2{}^7$
	$RAsX_2 + RX \longleftarrow$	$R_2AsX_3{}^9 \longleftarrow$	$R_2AsX + X_2{}^8$
III.	$R_2AsX + RX \longrightarrow$	$R_3AsX_2{}^{10} \longrightarrow$	$R_3As + X_2{}^{11}$
	$R_2AsX + RX \longleftarrow$	$R_3AsX_2{}^{13} \longleftarrow$	$R_3As + X_2{}^{12}$
IV.	$R_3As + RX \longrightarrow$	R_4AsX^{14}	
	$R_3As + RX \longleftarrow$	R_4AsX^{15}	
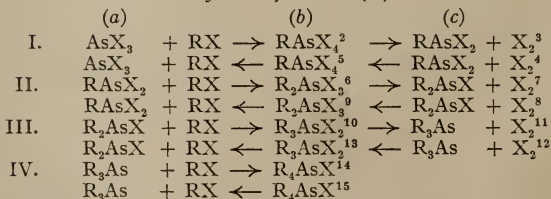
[1] This Journal, **35**, 5.
[2] See page 121.
[3] Evident in the presence of sodium.
[4] Ann. Chem. (Liebig), **107**, 274.
[5] *Ibid.*, **107**, 274.
[6] See page 107.
[7] Evident in the presence of sodium.
[8] Ann. Chem. (Liebig), **107**, 266.
[9] *Ibid.*, **107**, 269.
[10] Probable.
[11] Evident in the presence of sodium.
[12] Ann. Chem. (Liebig), **89**, 330; **112**, 231.
[13] *Ibid.*, **89**, 330.
[14] *Ibid.*, **112**, 230. Compt. rend., **39**, 541; **49**, 87. This Journal, **33**, 115.
[15] Ann. Chem. (Liebig), **89**, 311.

It will be observed that columns (a) and (c) involve trivalent arsenic, and column (b) pentavalent arsenic. Now, since it can be demonstrated that the compounds given are really formed in the order indicated, it is concluded that continuous progress through reactions I. to IV. involves a *regular alternation of tri- and pentavalent arsenic.*

This operation of a variable valency is further illustrated by the following

Hydrogen-Halogen-Alkyl Series (B).[1]

	(a)		(b)		(c)	
I.	AsH_3	$+ RX \rightarrow$	$RAsH_2X^2$ $\leftarrow$	$RAsH_2$	$+ HX^3$
II.	AsH_3	$+ RX \rightarrow$	$RAsH_3X$ $\rightarrow$	$RAsHX$	$+ H_2^4$
III.	$RAsH_2$	$+ RX \rightarrow$	$R_2AsH_2X^5$ $\leftarrow$	R_2AsH	$+ HX^6$
IV.	$RAsH_2$	$+ RX \rightarrow$	R_2AsH_2X $\rightarrow$	R_2AsX	$+ H_2^7$
V.	$RAsHX$	$+ RX \rightarrow$	$R_2AsHX_2^8$ $\leftarrow$	R_2AsH	$+ X_2^9$
VI.	$RAsHX$	$+ RX \rightarrow$	R_2AsHX_2 $\rightarrow$	R_2AsX	$+ HX^{10}$
VII.	R_2AsH	$+ RX \rightarrow$	R_3AsHX^{11} $\rightarrow$	R_3As	$+ HX^{12}$
			R_3AsHX $\leftarrow$	R_3As	$+ HX^{13}$
VIII.	R_2AsX	$+ RX \rightarrow$	$R_3AsX_2^{14}$ $\rightarrow$	R_3As	$+ X_2^{16}$
	R_2AsX	$+ RX \leftarrow$	$R_3AsX_2^{15}$ $\leftarrow$	R_3As	$+ X_2^{17}$
IX.	R_3As	$+ RX \rightarrow$	R_4AsX^{18}		
	R_3As	$+ RX \leftarrow$	R_4AsX^{19}		
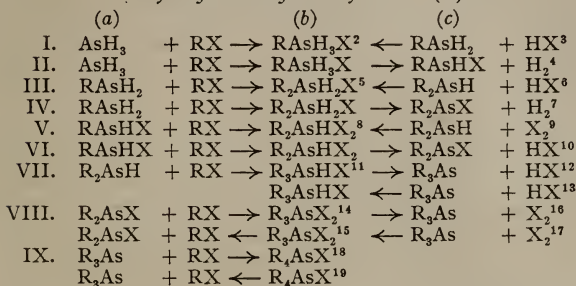
From the fact that most of the indicated reactions have been studied, and that their courses proceed as indicated by the arrows, general reversibility of reaction is very improbable.

Reactions I(a) and I(c) both yield the same product, $RH_2As\diagdown_X^H$, which decomposes as indicated in II(b). Reactions III(a) and III(c) yield the compound $R_2HAs\diagdown_X^H$,

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[1] It may be observed here that arsenic, unlike nitrogen, has a greater affinity for halogen than for hydrogen, and also for alkyl than for halogen or halogen acid.

[2] Not studied, but very probable, from analogy to the formation of primary arsine.

[3] *Vide* This Journal, **33**, 126; see pages 107 and 115.

[4] *Ibid.*

[5] *Vide ibid.*, **33**, 128; see page 107.

[6] *Vide ibid.*, **35**, 22-24.

[7] *Ibid.*

[8] Not studied.

[9] This Journal, **35**, 14-18.

[10] *Ibid.*

[11] *Ibid.*, **35**, 18-19; see pages 121, 122 and 123.

[12] *Ibid.*

[13] Not studied, but very probable.

[14] This Journal, **35**, 1.

[15] Ann. Chem. (Liebig), **112**, 228.

[16] Evident in the presence of sodium.

[17] Ann. Chem. (Liebig), **112**, 228.

[18] *Ibid.*

[19] *Ibid.*, **39**, 321. Also cf. page 112.

and this decomposes as shown in IV(*b*). Reaction V(*c*) and probably V(*a*) yield the product $R_2HAs{<}^X_X$, which decomposes as indicated in VI(*b*). Reactions VII(*a*) and VII(*c*) yield the compound $R_3As{<}^H_X$, which decomposes as represented in VII(*b*). Reactions VIII(*a*) and VIII(*c*) yield the product $R_3As{<}^X_X$, which probably reversibly decomposes as indicated in VIII(*a*). Reaction IX(*a*) yields the compound $R_3As{<}^R_X$, which decomposes as indicated in IX(*b*).

Now, since reactions I(*a*), III(*a*), VII(*a*), and VIII(*a*), as well as IX(*a*), all yield the compound R_4AsX in the presence of an *excess* of alkyl halide, it is concluded that the arsonium compound is formed by a series of *intermediate reactions involving molecular compounds which immediately or slowly dissociate, and that the process is repeated until the stable end products are formed.*[1]

As the result of a number of years of observation and study of the reactions of arsenic, the conviction has grown that the activity of this element cannot always be explained on the basis either of ionic or of kinetic-molecular mechanics. Briefly considered, this conviction has resulted from observation of the facts (1) that *most of the arsenic reactions are nonelectrolytic* or, in other words, they take place in the absence of water and (2) that, between the starting compounds and the most easily separated end product, there are observed *other* and

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[1] Analogous alternations of valency and formation of intermediate compounds are recognized in the reactions of the amine, phosphine, and stibine derivatives, as, for instance: (1) in the Hoffmann series of reactions, when alkyl iodides and ammonia are heated together and form a mixture of the four classes of amines; (2) when alkyl iodides are heated with phosphonium iodide in the presence of zinc oxide and form a mixture of primary and secondary phosphines; and (3) when alkyl iodides are treated with sodium antimonides and form tertiary and quaternary stibines. Ease of dissociation of the various molecular compounds determines the yields of the respective derivatives; in general, with the element nitrogen *primary* amines are formed in greater quantity; with phosphorus, *primary and secondary* phosphines; and with arsenic and antimony, the respective *quaternary* compounds are obtained in greater quantity.

usually *crystalline products*, which often can be separated and analyzed. Mention of these intermediate products has been made in previous contributions;[1] a systematic study is made herein to establish their frequent formation and to secure evidence leading to the general conclusion that *compounds of the element arsenic react largely by initial coalescence with the reagent*.

Whereas the nitrogen-organic and the oxygen-organic compounds yield intermediate products, their unstable properties and usually liquid condition prevent their easy and systematic study. The arsenic-organic compounds, on the other hand, containing the heavy element arsenic, usually form *crystalline* intermediate products which can often be separated and analyzed and therefore the arsenic derivatives offer a productive field for the study of chemical statics and dynamics.

Let us consider first, by way of illustration, the spontaneous oxidation of methylarsine by means of atmospheric oxygen:

$$CH_3AsH_2 + O_2 = CH_3AsO + H_2O,$$
$$2CH_3AsH_2 + 3O_2 = 2CH_3AsO(OH)_2.$$
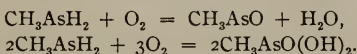
The first reaction is instantaneous, but the second is incomplete even after two weeks.

If applied here, Engler's theory of autoxidation[2] should involve *an initial addition of a molecule of oxygen*: $RH_2As{\scriptstyle\diagup O \atop \scriptstyle\diagdown O}$.

This "moloxide," by elimination of water, gives the end products, water and methylarsine oxide, $RAs = O$. It is not impossible, however, that the above peroxide form suffers a molecular rearrangement into the compound $RAs{\diagup OH \atop \diagdown OH}$ before splitting off water; confirmation of the probable formation of an addition product of the arsine and oxygen was deduced (1) from the observed absence of condensed vapors of water, proportional to the theoretical quantity, and (2) from the *slow* formation of methylarsonic acid, which, in accord-

[1] See THIS JOURNAL, **33**, 101; **35**, 1. J. Am. Chem. Soc., **28**, 347.
[2] C. Engler und J. Weissberg: Kritische Studien über die Vorgänge der Autoxydation (1904), 63.

ance with Engler's theory, could be formed in the manner indicated below:

$$(HO)_2RAs\cdots\cdots AsR(OH)_2.$$
$$\diagdown O-|-O\diagup$$
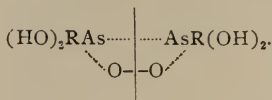
The analogous autoxidations of secondary arsines[1] are easily accounted for in the same manner:

$$R_2HAs\!\!<^{\diagup O}_{\diagdown O} \rightarrow R_2As\!\!<^{O-H}_{O} \quad \text{or} \quad \begin{array}{c} R_2As-H \\ | \\ O \\ | \\ O \\ R_2As-H \end{array} \rightarrow \begin{array}{c} R_2As\diagdown \\ R_2As\diagup \end{array}\!\!\!O + H_2O,$$
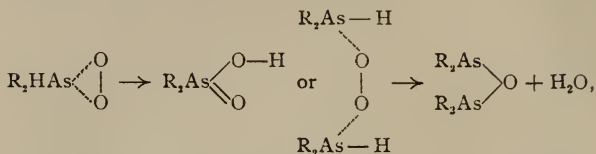
the addition of one molecule of oxygen to one molecule or to two molecules of the arsine determining whether cacodylic acid or cacodylic oxide is formed.[2]

The molecular rearrangement of the above-mentioned compounds, $RH_2As\!\!<^{\diagup O}_{\diagdown O}|$ and $R_2HAs\!\!<^{\diagup O}_{\diagdown O}|$, to form the compounds

$R-As\!\!<^{OH}_{OH}$ and $R_2As\!\!<^{OH}_{O}$, necessitates a *shifting of the hydrogen atoms*[3] *and a rearrangement of the oxygen valencies*, unless it is assumed that kinetic or ionic dissociations first take place as indicated below:

$$R-As\!\!<^{\diagup O}_{\diagdown O}| \quad \text{and} \quad R-As\!\!<^{\diagup O}_{\diagdown O}| \;;$$
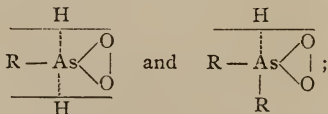
and that these dissociated parts readjust themselves.

[1] THIS JOURNAL, **35**, 9.

[2] Usually the two compounds are formed in nearly equal quantities. THIS JOURNAL, **35**, 14.

[3] Atomic shifting, an assumption not new in chemical statics and dynamics, cannot, of course, be dispensed with as an explanation of many reactions, particularly those included under tautomeric forms.

The latter hypothesis is unnecessary and, in fact, is untenable because it *assumes an effect without providing a probable cause*. We have only to conceive that the atoms of hydrogen, by virtue of kinetic motion and while being continuously held within the spheres of attraction,[1] pass to the intersection of the spheres of oxygen and arsenic attractions (Fig. I.), and then beyond the appreciable attraction of arsenic (Fig. II.). In this manner we come to an easy understanding of atomic shifting without employing any new theories or resorting to other than the fundamental assumptions of the science.
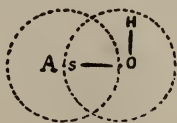
Fig. I.   Fig. II.

That *molecular coalescence is the inevitable preliminary condition of arsine reactions* is confirmed by the behavior of dimethylarsine with nitric acid.[2] *Normal* nitric acid (1 mol.) does not react with the arsine although the mixture is heated for one hour at 125°; *concentrated* nitric acid (1 mol.) reacts with explosive violence. In the former case, the nitric acid is *ionized*; in the latter, its condition is *molecular*. In other words, the compound H—O—NO$_2$ has, but the group —O—NO$_2$ has not, the property of *adding to the arsine* and of yielding the end product, cacodylic acid. If the doubly bound oxygen atoms of the nitrate group were the active portion, then both ionic and molecular nitric acid should react; however, since only molecular nitric acid reacts, only the H—O—N part of the acid offers hope of a satisfactory explanation. If initial molecular coalescence is the indispensable criterion, then the following preliminary mechanics are conceivable:

[1] Mechanical arrangements and invariability of quantity and position are, of course, improbable conceptions of valency.

[2] This Journal, **35,** 27.

$$R_2As — H$$
$$\|$$
$$\|$$
$$H — O — NO_2$$

$$\rightarrow \quad R_2As — H$$
$$HO \diagup \diagdown NO_2 ,$$
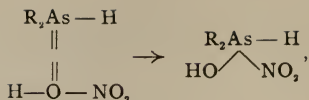
dimethylarsine nitrate[1] being first formed.

Since the formation of the analogous *arsine salt*,

$$[(CH_3)_2AsH]_2.H_2SO_4,$$
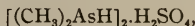
was proven in the case of sulphuric acid,[2] the probable forma-

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[1] Objections may be raised as to the structure of this salt, on the grounds that it is not strictly analogous to the structure of ammonium nitrate, $H_4N—O—NO_2$; however, there is no evidence that these salts are strictly analogous. The fact that hydroxyl attached to arsenic constitutes a more stable combination than hydrogen attached to arsenic, the reverse being true in the case of nitrogen, argues a difference in these salts.

Since, in the case of ammonia and hydrochloric acid, at least a trace of water is necessary (Hughes: Phil. Mag., **35**, 53; Baker: J. Chem. Soc., **65**, 611) to form ammonium chloride, it is usually held that ionized hydrochloric acid adds to ammonia; of course, kinetic dissociation is precluded for the reason that hydrochloric acid does not begin to dissociate below 1000° (Ber. d. chem. Ges., **6**, 423). However, initial ionic or kinetic dissociations are not the only possible explanations of these phenomena; the water that is necessary may add in the following manner:

$$\begin{array}{c} H \\ | \\ H_3N= =O \\ | \\ H \end{array} \longrightarrow NH_4OH;$$
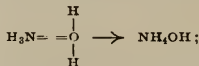
and then the acid and base may react, either through their ions, or as indicated below:

$$\begin{array}{c} Cl \\ | \\ H_4N—O= =Cl \longrightarrow H_4N—O—H \longrightarrow H_4N—Cl + HOH. \\ |\ \ | \qquad\qquad | \\ H\ \ H \qquad\qquad\ H \end{array}$$
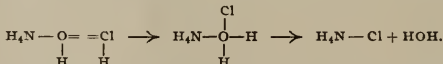
That the ions of water first add to ammonia is rendered improbable from the fact that NH_3 *itself is not an ion.*

When water acts on calcium oxide and other oxides of both metals and nonmetals, it is difficult to conceive of the mechanics of the action on the basis of ionization since the oxides themselves are not ions and water is ionized to the extent of only 2 mg. of hydrogen to a ton of water. Furthermore, kinetic action is precluded because water does not decompose below 1000°. In accordance with the above principles, however, the action is readily explained as follows:

$$Ca=O= =O—H \longrightarrow Ca \diagup OH \diagdown OH .$$
$$|$$
$$H$$
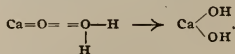
Whereas *molecular affinity* is recognized in hydrated salts and other compounds, its rational application here necessitates an assumption of the *tetravalency* of oxygen. The position of oxygen in the periodic system, the variability of valency of its closest analogue, sulphur, and the necessary postulate of a higher valency of oxygen to explain water of crystallization and the addition products of alcohols, ethers, etc., clearly entitles oxygen to an occasional higher valency than two.

[2] THIS JOURNAL, **35**, 24.

tion of the nitrate is easily deduced. The sulphate gave, as
the main end products, cacodyl sulphide (and cacodylic acid),

$$(CH_3)_2As—H$$

therefore, the structure
$$\begin{matrix} H—O \\ H—O \end{matrix} \Big\rangle SO_4$$
is probable, *sul-*

$$(CH_3)_2As—H$$
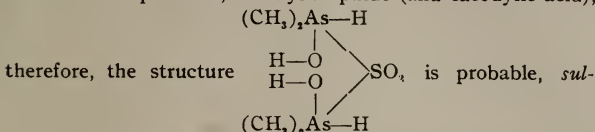
phur being bound to arsenic. Analogously, *nitrogen is prob-
ably bound directly to arsenic*, as is shown in the formula
$(CH_3)_2As—H$
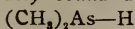
$$H—O \quad NO_2$$
. Under the influence of heat[1] (internal kinetic

dissociation), this compound could split off nitrous acid,

$$(CH_3)_2As\text{------}H \qquad (CH_3)_2As + H$$
$$\begin{matrix} & | & & & | \\ & O & \to & & O \\ HO & NO & & H—O & NO \end{matrix},$$
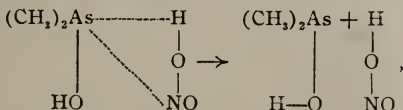
forming dimethylhydroxylarsine,[2] which would react with
more nitric acid, as follows:

$$(CH_3)_2As—O—H \longrightarrow (CH_3)_2As—OH \longrightarrow$$
$$\begin{matrix} \| & & & & \\ H—O—N\diagup^{O}_{\diagdown O} & & HO \diagup \diagdown N \diagup^{O}_{\diagdown O} \end{matrix}$$

$$(CH_3)_2As = O\text{-----}H \longrightarrow (RH_3)_2As = O \qquad H$$
$$\begin{matrix} \diagup \diagdown \diagup & & | & + & O \\ H—O \quad N = O & & H—O & & N = O; \end{matrix}$$
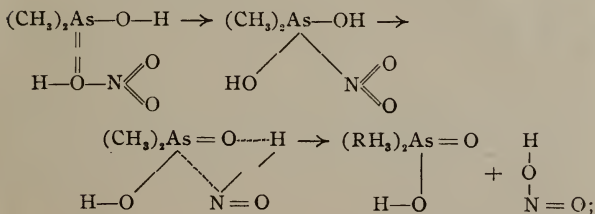
and thus satisfactorily explain the formation of cacodylic
acid, the main end product.

The above described action of nitric acid illustrates that

[1] It must be remembered that dissociations may be induced not only by heat,
light, and other forces, but also by various reagents. Since the latter really involve
other chemical changes the term *dissociation* is used herein to indicate decompositions
induced by heat only.

[2] This compound probably has no separate existence since, under conditions
favoring its formation, its anhydrous form, cacodylic oxide, $R_2AsOAsR_2$, is always
obtained (Baeyer: Ann. Chem. (Liebig), **107**, 282). However, since cacodylic oxide
is proved (THIS JOURNAL, **35**, 9–14) to be an oxidation product of dimethylarsine
the above conclusions are justified.

the process of oxidation is conditioned, not by the mere presence
of oxygen but by a facility of coalescence of the reagent with the
substance; in other words, the reducing power of the arsines
and their derivatives is conditioned by a capacity for pre-
liminary molecular linking; at any rate, most reduction pro-
cesses of the arsines thus far studied[1] have yielded initial molec-
ular aggregates, or have given evidence of their formation.

A striking example of this action of the arsenic atom is
observed in the formation of arsonic acids, when sodium
arsenite is treated with alkyl iodides. The reaction

$$Na_3AsO_3 + RI \longrightarrow RAsO_3Na_2 + NaI$$
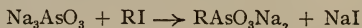
was discovered by Meyer[2] and was described by him as "an
anomalous reaction," because by "double decomposition" it
was expected that an alkyloxy compound would be formed.
However, it was found that the alkyl group combines di-
rectly with the arsenic. This is easily explained on the basis
of initial molecular attraction; the arsenite and the halide
uniting, rearranging, and decomposing as follows:
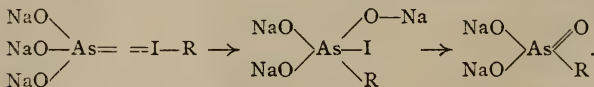
Thus it is seen that instead of being an "anomalous reaction"
it may be considered a beautiful example of the *normal reaction.*

From the foregoing it is concluded that many reactions of
the arsine compounds can best be explained by making the
following assumptions:

1. Unsaturated valencies (partial or latent valencies) in
both substances;

2. Molecular coalescence of the two substances;

3. A condition of instability established in the molar ag-
gregate, owing to this distribution of the total valencies of the
nuclear elements, and thus inducing either

4. A tendency toward reversible reaction or

5. A tendency toward rearrangement; and finally,

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[1] See page 97.
[2] Ber. d. chem. Ges., **16**, 1441.

6. A dissociation of the molar aggregate into its more stable components.

<div align="center">EXPERIMENTAL.</div>

1. Electrolytic Reduction of Arsine Derivatives.

These experiments were undertaken for the purpose of demonstrating the formation of intermediate products when alkyl arsenic derivatives are reduced to free arsines. It was found hitherto that the final reduction product of both cacodyl chloride[1] and cacodyl[2] is dimethylarsine; it is now proposed to show that cacodyl is an intermediate product of the reduction of cacodyl chloride, and that the successive reactions are as follows:

$$2(CH_3)_2AsCl + 2H = (CH_3)_2As—As(CH_3)_2 + 2HCl,$$
$$(CH_3)_2As—As(CH_3)_2 + 2H = 2(CH_3)_2AsH.$$
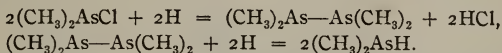
After a number of unsuccessful experiments with porous cells used to keep the anode and cathode solutions separate, a cell was devised which was found most convenient, not only for observing the progress of the reductions but also for experimenting with small quantities of material. The apparatus used is shown in Fig. III.

The other details are as follows: (*a*) platinum cathode spiral, (*b*) porous clay partition, (*c*) a packed asbestos ring, (*d*) platinum anode plate, (*e*) glass support for the anode plate, (*f*) exit for anode gas and intake for anode solution, (*g*) drain for anode solution, (*h*) exit for cathode gas, (*i*) intake for cathode solution.

Method of Using.—The cathode solution first used was prepared by mixing 5 grams of cacodyl chloride, 90 grams of formic acid, and 8 grams of alcohol; its specific gravity was 1.08. An anode solution of the same specific gravity was prepared from sulphuric acid. After sufficient anode solution and 11 cc. of cathode solution were run into the reduction cell and all the parts of the apparatus were adjusted, a current of 5 to 6 volts and 0.5 to 0.6 ampere was turned on. The cathode solution clouded almost immediately and after 500

[1] Ber. d. chem. Ges., **27**, 1378.
[2] This Journal, **35**, 3.

cc. of electrolytic hydrogen had been evolved in the voltameter, a heavy oil was found to have separated in the cell and a spontaneously inflammable gas *began* to be evolved with the cathode hydrogen—this gas increased in concentration during the remainder of the reduction. The oil, insoluble in formic acid, was identified as cacodyl; the gas was found to be dimethylarsine; hence the above equations are established.
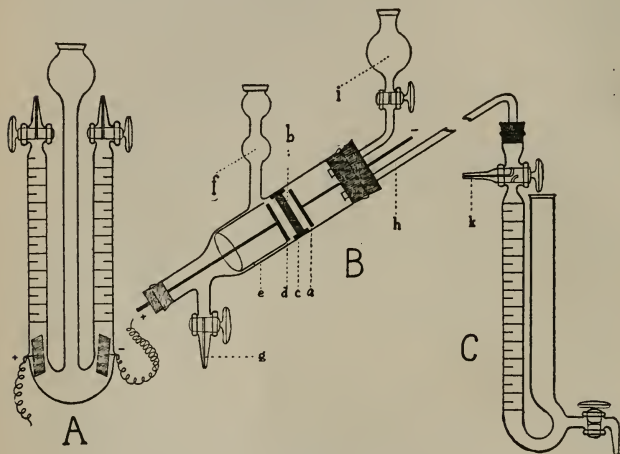
Fig. III.

A. A Hofmann U-tube placed in series with the cell and used as a hydrogen voltameter.
B. The reduction cell, made of glass.
C. Apparatus used to measure the gas evolved at the cathode and subsequently to deliver into Hempel burettes (at point *k*).

The following experiment was undertaken for the purpose of determining the relative rates of reduction of cacodyl chloride to cacodyl, and of the latter to dimethylarsine:

The cathode solution was prepared by dissolving 9.1 grams of cacodyl chloride in a mixture of 90 cc. of alcohol and 25 cc. of hydrochloric acid (sp. gr. 1.2); one fifth of this solution and a current of 5 to 6 volts and 1.05 to 1.20 amperes were used for the reduction. When exactly 50 cc. of hydrogen had

been evolved in the voltameter (II.), the current was turned off and the volume of mixed gases (III.) evolved from the cathode solution was measured in the apparatus C; the gas was next drawn over into a Hempel burette containing silver nitrate solution and, after shaking, the volume of the residual gas (unfixed hydrogen) was measured (V.) The loss in volume at this point represented an equivalent volume of dimethylarsine gas and one half of this volume was equivalent to the volume of hydrogen fixed by dimethylarsine. Fifty cc. of hydrogen, minus the volume of unfixed residual hydrogen and the hydrogen fixed by dimethylarsine, represented the volume of hydrogen fixed by cacodyl, according to the equation

$$2(CH_3)_2AsCl + H_2 = [(CH_3)_2As]_2 + 2HCl.$$
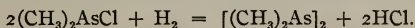
Reduction of Cacodyl Chloride.

I. No. of experiment.	II. Total hydrogen.	III. Burette gas.	IV. 50 cc. minus burette gas.	V. Residual gas (AgNO₃).	VI. Dimethylarsine.	VII. Hydrogen fixed by (CH₃)₂AsH.	VIII. Hydrogen fixed by cacodyl.
1	50	2.5	47.5	2.5	0.0	0.0	47.5
2	100	5.1	44.9	5.0	0.1	0.0	45.0
3	150	7.9	42.1	7.9	0.0	0.0	42.1
4	200	11.9	38.1	11.8	0.1	0.1	38.1
5	250	15.9	34.1	15.7	0.2	0.1	34.2
6	300	20.4	29.6	19.7	0.7	0.3	30.0
7	350	25.0	25.0	24.2	0.8	0.4	25.4
8	400	30.4	19.6	29.3	1.1	0.6	20.1
9	450	36.3	13.7	34.3	2.0	1.0	14.7
10	500	41.3	8.7	38.9	2.4	1.2	9.9
11	550	44.5	5.5	40.5	4.0	2.0	7.5
12	600	45.3	4.7	39.6	5.7	2.9	7.5
13	650	47.5	2.5	40.4	7.1	3.6	6.0
14	700	48.6	1.4	41.2	7.4	3.7	5.1
15	750	50.1	—0.1	40.9	9.2	4.6	4.5
16	800	50.8	—0.8	40.7	10.1	5.1	4.2
17	850	52.2	—2.2	41.9	10.3	5.2	2.9
18	900	52.2	—2.2	42.2	10.0	5.0	2.8
19	950	52.4	—2.4	42.2	10.2	5.1	2.7
20	1000	52.2	—2.2	42.1	10.1	5.0	2.9
22	1100	52.0	—2.0	42.8	9.2	4.6	2.6
24	1200	51.0	—1.0	43.9	7.1	3.5	2.6
26	1300	50.9	—0.9	45.1	5.8	2.8	2.1
28	1400	51.0	—1.0	45.9	5.1	2.6	1.5
30	1500	51.5	—1.5	47.0	3.5	1.7	1.3
32	1600	50.7	—0.7	48.2	2.5	1.2	0.6
34	1700	50.1	—0.1	49.0	1.1	0.6	0.4

It may be observed in the table: that the volume of gases evolved from the cathode solution, at first, is much less than the volume of the voltameter hydrogen collected during the same interval of reduction; then, at about the middle of the series of reductions, it becomes equal to the voltameter hydrogen; during most of the remainder of the reductions, the cathode gas volume is greater than the voltameter hydrogen; but finally, it becomes just equal to it. When cacodyl alone is formed, the residual hydrogen must be less than the voltameter hydrogen, owing to the *fixing* of hydrogen (the product being hydrochloric acid), as shown in the above equation. When dimethylarsine alone is formed by the reaction, .

$$(CH_3)_2As—As(CH_3)_2 + H_2 = 2(CH_3)_2AsH,$$
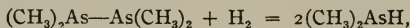
the total volume of gas evolved must be greater than the voltameter hydrogen—two volumes of arsine resulting from one volume of hydrogen. Therefore, when both cacodyl and dimethylarsine are being formed, the burette gas represents the algebraic sum of these two reductions; and, depending upon the proportion of the two products, may be less or greater than the voltameter hydrogen. With the cubic centimeters of "fixed" hydrogen as ordinates and the quantity of electricity, measured in 50 cc. of hydrogen, as abscissas, (1) the composite curve of reduction, (2) the dimethylarsine curve, and (3) the cacodyl curve may be plotted, as shown in Fig. IV.

It will be seen that when the composite curve of reduction crosses the base line, the quantity of arsine is just twice that of the cacodyl.

As plotted, the area included within the cacodyl and dimethylarsine curves represents the total quantity of *hydrogen fixed*; the area included between the base line and a parallel line at 50 cc. represents the total *electrolytic hydrogen*.

From a consideration of the above experiments it may be anticipated that when cacodyl itself is reduced, the *composite curve* of reduction becomes coincident with the dimethylarsine curve. This is confirmed by the following experiment. A cathode solution was prepared by dissolving 5 cc. of crude cacodyl
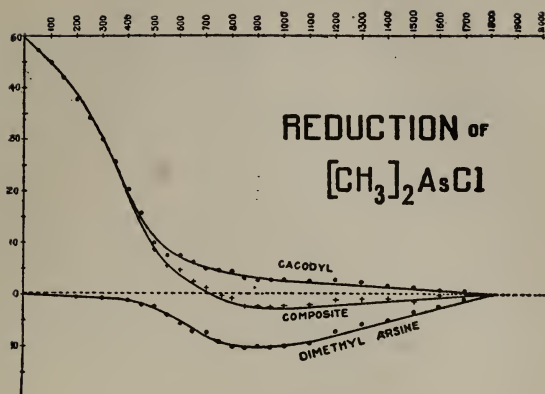
Fig. IV.

in a mixture of 50 cc. of alcohol and 25 cc. of hydrochloric acid (sp. gr. 1.20). With a current of 5 to 6 volts and 1.0 to 0.6 ampere, 20 cc. of this solution were reduced in the manner described above.

Reduction of Cacodyl.

I.	II.	III.	IV.	V.	VI.
Number of experiment.	Total hydrogen.	Burette gas.	50 cc. minus burette gas.	Residual gas (AgNO₃).	Dimethyl-arsine.
1	50	36.0	14.0	36.0	0.0
2	100	37.4	12.6	37.3	0.1
3	150	38.9	11.1	38.5	0.4
4	200	40.3	9.7	39.6	0.7
5	250	41.8	8.2	41.1	0.7
6	300	43.6	6.4	42.6	1.0
7	350	46.2	3.8	44.8	1.4
8	400	47.6	2.4	45.7	1.9
9	450	49.1	0.9	46.6	2.5
10	500	50.4	—0.4	47.0	3.4
11	550	52.0	—2.0	48.0	4.0
12	600	52.8	—2.8	49.0	3.8
13	650	54.0	—4.0	49.0	5.0
14	700	55.0	—5.0	49.8	5.2
15	750	55.6	—5.6	50.1	5.5

Reduction of Cacodyl—(Continued).

I. Number of experiment.	II. Total hydrogen.	III. Burette gas.	IV. 50 cc. minus burette gas.	V. Residual gas (AgNO₃).	VI. Dimethyl-arsine.
16	800	55.9	—5.9	50.3	5.6
17	850	55.8	—5.8	50.3	5.5
18	900	55.7	—5.7	50.3	5.4
20	1000	55.1	—5.1	50.5	4.6
22	1100	53.9	—3.9	49.9	4.0
24	1200	52.8	—2.8	49.8	3.0
26	1300	51.8	—1.8	49.8	2.0
28	1400	50.8	—0.8	49.9	0.9
30	1500	50.2	+0.2	50.1	0.1

REDUCTION OF CACODYL

COMPOSITE
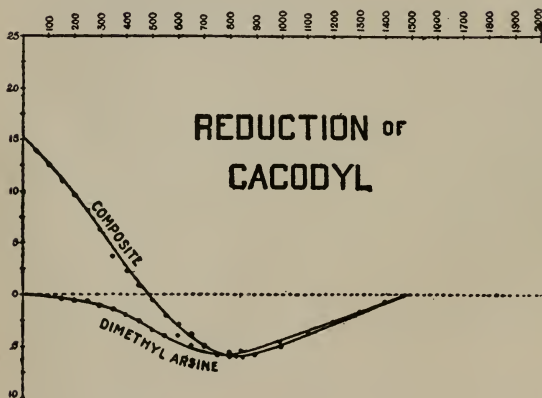
DIMETHYL ARSINE

Fig. V.

That the burette readings were not immediately greater than the voltameter readings or, in other words, that the composite curve of reduction was not more nearly coincident with the dimethylarsine curve, is explained by the facts (1) that it is almost impossible to prepare and to handle pure cacodyl without its becoming oxidized, (2) crude cacodyl contains large quantities of cacodylic oxide, and (3) dimethyl-arsine is somewhat soluble in the above mentioned cathode

solution. However, the curves show sufficiently well that cacodyl is electrolytically reduced to dimethylarsine.

In view of the above experiments and since dimethylarsine is easily prepared from cacodylic acid by reduction with zinc and hydrochloric acid, it might be supposed that the electric current would induce the same reaction:

$$(CH_3)_2AsOOH + 4H = (CH_3)_2AsH + 2H_2O.$$

However, experiments showed that no arsine was evolved; an explanation of this is seen in the following equations:

$$(CH_3)_2AsO_2H = (CH_3)_2As\overset{-}{O}_2 + \overset{+}{H},$$
$$2(CH_3)_2AsO_2 + H_2O = 2(CH_3)_2AsO_2H + O.$$
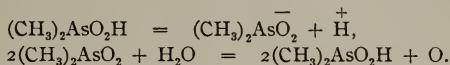
II. Primary Arsines.

With ELRICK WILLIAMS.

Studies with Gaseous Primary Methylarsine.

The sodium salt of methylarsonic acid[1] was reduced by zinc and hydrochloric acid[2] and the mixture of hydrogen and gaseous methylarsine was passed into a large bottle filled with water and so arranged that the gaseous mixture could both be preserved free from oxidation and also so that portions of it, as desired, could be drawn off into Hempel burettes. Usually the gaseous mixture was drawn out by depressing the companion tube of the Hempel burette; then boiled water was permitted to run into the gas reservoir, so as to equalize the interior and exterior pressures. Samples of the gas in the Hempel tube were treated with solutions as indicated in the following table of preliminary experiments; from time to time the concentration of the arsine in the reservoir was determined by treatment with silver nitrate solution.[3]

[1] Ann. Chem. (Liebig), **249,** 147.
[2] THIS JOURNAL, **33,** 120.
[3] *Ibid.,* **33,** 125.

Reactions of Monomethylarsine.

Exp. No.	Reagent, aqueous solution.	Volume of gas taken.	Volume loss resulting.	Per cent of loss.	Known per cent of arsine.	Time in minutes.	Observations and remarks.
1	$KMnO_4$	88.8	12.2	13.8	13.10	3–5	Brown black precipitate; odorless product; acid reaction.
2	$KMnO_4$	87.7	10.7	12.2	12.80	3–5	Precipitate lost 24.10 per cent on igniting.
3	$K_3Fe(CN)_6$	91.8	9.5	10.34	10.35	30	Sol. yellow; white precipitate; odor RAsO and HCN.
4	$FeCl_3$	86.0	8.7	10.10	10.20	30+	Sol. green; white precipitate; odor RAsO.
5	$Pb(Ac)_2$	86.3	5.9	6.80	6.60	60	Reaction slow; black precipitate; odorless.
6	$K_2Cr_2O_7$	92.0	9.8	10.60	10.35	10	Sol. darkened; product odorless.
7	H_2CrO_4	96.0	20.4	21.25	21.20	2–3	Same as Exp. 6.
8	H_2O_2	93.3	2.9	3.10	10.35	60	O_2 evolved; cloudy sol.; $\frac{1}{2}RAsH_2$ remained.
9	Br_2	92.4	9.6	10.60	10.35	1–2	*White solid; then clear, odorless solution.*
10	$HgCl_2$	87.0	9.3	10.70	10.35	1–2	White; *then silky, golden solid; brown red;* darker.
11	$CuSO_4$	86.9	7.0	8.05	9.02	1–2	Blueness lost; *red brown, silky solid* formed.
12	HNO_2	92.4	9.5	10.29	10.35	3–5	NO and $RASO_3H_2$ formed.
13	conc. H_2SO_4	72.1	11.4	15.81	19.17	1–2	Light yellow solid; SO_2 but no H_2S.
14	conc. HNO_3	95.1	15.9	16.72	21.20	1–2	N_2 or N_2O formed; RAsO and $RAsO_3H_2$.
15	$SbCl_3$	77.8	5.8	7.15	7.50	1–2	*Silky, white solid;* then yellow; finally amorphous; red.
16	$AsCl_3$	92.4	21.0	22.70	21.20	3–5	Residual gas free from arsenic.
17	KdCl	93.6	19.7	21.05	21.20	30	Residual gas fumed.
18	Kd-Kd	77.8	17.2	21.11	21.20	30	Fumed, of course.
19	$SnCl_4$	93.0	19.9	21.40	21.20	3–5	*Yellow white solid;* yellow oil; residual gas contained arsenic.
20	PCl_3	61.2	8.2	13.40	13.75	5	Orange solid; residual gas free from arsenic.
21	S_2Cl_2	98.4	19.8	20.12	21.20	5	Yellow cheeselike solid; residual gas contained S.
22	SO_2	71.8	4.8	6.69	7.00	60	Opaque sol.; no H_2S in residual gas.
23	PbO_2	81.5	14.0	17.19	21.20	4000	Red brown solid; filtered sol. contained Pb.

Interpretations of the above data render probable the following equations:

1. $6KMnO_4 + 5RAsH_2 =$
$$6MnO + 3RAsO_3K_2 + 2RAsO_3H_2 + 3H_2O.$$

2. $6KMnO_4 + 5RAsH_2 =$
$$4MnO + 3RAsO_3K_2 + 2RAsO_3Mn + 5H_2O.$$

3. $4K_3Fe(CN)_6 + RAsH_2 + H_2O =$
$$3K_4Fe(CN)_6 + H_4Fe(CN)_6 + RAsO.[1]$$

4. $4FeCl_3 + RAsH_2 + H_2O = 4FeCl_2 + 4HCl + RAsO.[2]$

5. $4Pb(AC)_2 + RAsH_2 + 3H_2O =$
$$3Pb + 8HC_2H_3O_2 + RAsO_3Pb.[2]$$

6. $K_2Cr_2O_7 + RAsH_2 =$ (See This Journal, **35**, 28).

7. $6H_2CrO_4 + 2RAsH_2 =$
$$3(2CrO_2.H_2O) + 2RAsO_3H_2 + 3H_2O.[3]$$

8. $2H_2O_2 + RAsH_2 = RAsO + 3H_2O.$

9. $3Br_2 + RAsH_2 + 3H_2O = RAsO_3H_2 + 6HBr.[4]$

10. $HgCl_2 + RAsH_2 = RAsHHgCl.HCl$ (etc.).[5]

11. $CuSO_4 + RAsH_2 = RAsH_2.CuSO_4(?),$

12. $6HNO_2 + RAsH_2 = RAsO_3H_2 + 6NO + 3H_2O.[6]$

13. $H_2SO_4 + RAsH_2 = RAsH_2.H_2SO_4.[7]$

14. $HNO_3 + RAsH_2 =$ (See This Journal, **33**, 125; **35**, 27).

15. $SbCl_3 + RAsH_2 =$ (See page 112).

16. $AsCl_3 + RAsH_2 =$ See page 111).

17. $(CH_3)_2AsCl + RAsH_2 =$ (See page 122).

18. $(CH_3)_2AsAs(CH_3)_2 + RAsH_2 =$ No reaction.

19. $SnCl_4 + RAsH_2 =$ (See page 110).

20. $PCl_3 + RAsH_2 =$ (See page 111).

21. $S_2Cl_2 + RAsH_2 = RAsCl_2 + S + H_2S.[8]$

22. $SO_2 + RAsH_2 =$ (See This Journal, **35**, 38).

23. $PbO_2 + RAsH_2 =$ (See This Journal, **35**, 30).

[1] Cf. This Journal **35**, 35.
[2] *Ibid.*, **35**, 30.
[3] *Ibid.*, **35**, 28.
[4] *Ibid.*, **33**, 126; **35**, 14.
[5] *Ibid.*, **33**, 127; **35**, 35.
[6] *Ibid.*, **35**, 26.
[7] *Ibid.*, **35**, 24.
[8] *Ibid.*, **35**, 39.

Monomethylarsine and Gases.

Exp. No.	Gas	Volume of gas	Volume RAsH₂ mixture	Volume of contained RAsH₂	Volume loss	Ratio loss to RAsH₂	Time. Min.	Observations and remarks.
1	O_2	24.3	60.7	4.4	11.0	2.5	30	White solid; then brick red with white.
2	O_2	32.4	64.0	4.6	10.2	2.3	30	Shaking 20 minutes—loss 2.2 cc.; letting stand 1 minute—loss 3 cc. more; water retards oxidation.
3	N_2O	29.7	62.6	4.5	0.2		30	Residual gas yielded RAsH₂.
4	NO	50.1	61.0	4.4	1.0		30	Residual gas showed NO and RAsH₂.
5	NO_2	30.5	47.3	3.1	6.3	2.0	5	Residual gas showed NO but no RAsH₂.

These reactions are probably represented by the following equations:

1. $3O_2 + 2RAsH_2 = 2RAsO_3H_2$ (ratio 2.5 : 1).
   $2O_2 + 4RAsH_2 = (RAs)_4 + 4H_2O$ (ratio 1.5 : 1).[1]
2. $O_2 + RAsH_2 = RAsO + H_2O$ (ratio 1 : 1).
3. $N_2O + RAsH_2 =$ no reaction.[2]
4. $NO + RAsH_2 =$ no reaction.[3]
5. $3NO_2 + RAsH_2 = 3NO + RAsO_3H_2$.

[1] See This Journal, **35**, 9.
[2] Ibid., **35**, 25.
[3] Ibid., **35**, 26.

Hydriodic Acid and Methylarsine.—A mixture of 50.4 cc. of gaseous methylarsine (8.1 cc.) and hydrogen (42.3 cc.), treated over mercury with 1 cc. of concentrated aqueous hydriodic acid, *increased* 2 cc. in volume in 20 minutes; after heating for 20 minutes more at 100°, an increase of 10.9 cc. in volume resulted. The gaseous mixture, after cooling to the original temperature, was treated with a solution of silver nitrate—a decrease in volume of 6.7 cc. resulted. From these experiments it is concluded that the following reactions are slow[1] or are easily reversible:

$$CH_3AsH_2 + HI \rightleftarrows CH_3AsH_3I \rightarrow CH_3AsHI + H_2,$$
$$CH_3AsHI + HI \rightleftarrows CH_3AsH_2I_2 \rightarrow CH_3AsI_2 + H_2.$$
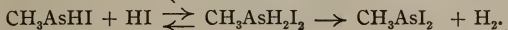
Propyl Iodide and Methylarsine.—When a gaseous mixture of 75.5 cc. of methylarsine (10.1 cc.) and hydrogen (63.4 cc.), with 1 cc. of liquid *n*-propyl iodide, was heated for one hour at 100° in a mercury eudiometer, a decrease in volume of 4 cc. was observed on cooling to the original temperature. When treated with silver nitrate solution, the residual gas suffered a loss of 5.8 cc. (unchanged methylarsine). During the experiment, *light yellow crystals* (melting below 100°) were observed on the walls of the eudiometer; therefore the following equation is justified:[2]

$$CH_3AsH_2 + C_3H_7I \rightleftarrows (CH_3)(C_3H_7)AsH_2I.$$
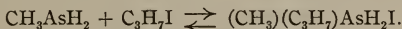
Silver Nitrate and Methylarsine.[3]—The black precipitate in a gas burette, after treatment of a silver nitrate solution with quantities of methylarsine, was washed with water and dried at 100°.

0.5439 gram of substance gave 0.4430 gram of AgCl.

	Calculated for $CH_3AsO_3Ag_2$.	Found.
Ag	60.69	79.90

Since methylarsonic acid was found in the precipitate, the latter is evidently a mixture of metallic silver and silver methylarsonate.

[1] Cf. This Journal, **35**, 27.
[2] Addition products are almost invariably observed when primary, secondary, and tertiary arsines are treated with alkyl iodides. Cf. This Journal, **33**, 128, and see pages 121, 122, and 123.
[3] Cf. This Journal, **33**, 126; **35**, 35.

Methylarsine Oxide and Methylarsine.—When the white methylarsine oxide, formed on the walls of a Hempel burette by the reaction of atmospheric oxygen with methylarsine, was treated with gaseous methylarsine, all of the methylarsine was fixed and a brick red solid replaced the white oxide. Evidently the following reaction:

$$2CH_3AsO + 2CH_3AsH_2 \longrightarrow (CH_3As)_4 + 2H_2O;$$
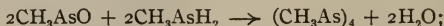
explains the formation of the red polymers always formed by the spontaneous oxidation of the arsines. The details of the reaction are shown as follows:

$$\begin{array}{ccc} CH_3-As=O & CH_3-As-OH & CH_3-As \\ \overset{\shortparallel}{CH_3}-\overset{\shortparallel}{As}=H_2 & \longrightarrow \quad CH_3-As-H & \longrightarrow \quad CH_3-As \end{array} + H_2O;$$
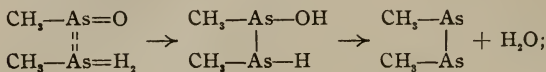
two groups, $CH_3-As-As-CH_3$, condensing and evidently forming $CH_3-As-As-CH_3$
$$\begin{array}{c} | \quad | \\ CH_3-As-As-CH_3 \end{array}.$$
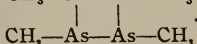
The following substances failed to react with gaseous methylarsine: hydrogen sulphide, yellow ammonium sulphide, potassium nitrite, potassium hydroxide, nickelous chloride, formaldehyde, acetic acid, aniline, nitrobenzene, and benzotrichloride.

Reactions of Ethylarsine.

Iodine.—When equimolecular quantities of the two substances were brought together in a sealed tube containing ether, the color of the iodine was quickly discharged and a golden yellow solution resulted. Hydrogen and an oil boiling at 205° to 210° and containing 63.8 per cent of iodine (calculated for $C_2H_5AsI_2$[1] is 70.9 per cent) were obtained. The following equation is justified:

$$C_2H_5AsH_2 + I_2 = C_2H_5AsI_2 + H_2.$$

Bromine.—When equimolecular quantities of ethylarsine and bromine were brought together in ether, a *red brown, amorphous solid* was formed immediately and remained permanently (one year) undissolved. Considerable pressure (hydrogen)

[1] Ann. Chem. (Liebig), **110**, 367.

was observed on opening the tube; the ether solution yielded, by distillation, an oil, *ethylarsine dibromide*, boiling at 192°.

0.4120 gram substance gave 0.5812 gram AgBr.

	Calculated for $C_2H_5AsBr_2$.	Found.
Br	60.60	60.03

When treated with platinic chloride the dibromide liberated heat and slowly formed yellow white crystals, which were dried on the water bath and ignited.

0.8622 gram substance gave 0.2700 gram Pt.

	Calculated for $C_2H_5AsBr_2.PtCl_4$.[1]	Found.
Pt	32.68	31.31

The brown residue from the sealed tube experiment was analyzed:

0.1865 gram substance gave 0.0260 gram AgBr.
0.2106 " " " 0.2247 gram $Mg_2As_2O_7$.

	Calculated for		Found.
	$(C_2H_5As)_4$.	C_2H_5AsHBr.	
Br	0.00	43.24	10.25
As	72.11	40.54	51.62

Evidently this substance is a mixture. The end reaction of the arsine with bromine is as follows:

$$C_2H_5AsH_2 + Br_2 = C_2H_5AsBr_2 + H_2;$$
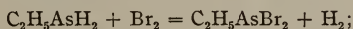
while positive evidence of intermediate products is deduced.

Sulphur.—When 2 grams of ethylarsine (1 mol.) and 1.2 grams of sulphur (2 atoms) were brought together in a sealed tube filled with carbon dioxide, the sulphur was seen to dissolve rapidly, and to yield a viscid, colorless liquid. On opening the tube, great pressure (hydrogen sulphide, but no hydrogen) was observed. The percentage of sulphur in the gluelike mass was determined:

0.1962 gram substance gave 0.3475 gram $BaSO_4$.

	Calculated for		Found.
	$C_2H_5AsS_2$.	C_2H_5AsS.	
S	38.09	23.52	24.28

[1] Cf. This Journal, **35**, 32.

Evidently the substance is *ethylarsine sulphide* with an admixture of free sulphur or the disulphide, and the original reaction is as follows:

$$C_2H_5AsH_2 + S_2 = C_2H_5AsS + H_2S.$$

Mercuric Chloride.—When equimolecular quantities of the two substances were brought together in a sealed tube filled with carbon dioxide, a dark *yellow black precipitate* formed immediately and changed after a time to a compact, finely divided, black precipitate. On opening the tube no hydrogen or mercurous chloride, but gaseous hydrochloric acid and metallic mercury were found. An ether solution of the oil became yellow red in the air and ethylarsine dichloride was detected in the ether solution, therefore the final reaction is expressed by the following equation:[1]

$$C_2H_5AsH_2 + 2HgCl_2 = C_2H_5AsCl_2 + 2Hg + 2HCl.$$

Mercuric Iodide.—When 2.5 grams of ethylarsine (1 mol.) and 10.7 grams of mercuric iodide (1 mol.) were brought together in ether contained in a sealed tube, a *bright yellow product* was formed immediately. On opening the tube hydrogen, mercurous iodide (4 grams—calculated, 7.7 grams), and an oil (5.7 grams) were obtained; the oil showed the presence of ethylarsine diiodide, therefore the reaction here is as follows:

$$C_2H_5AsH_2 + 2HgI_2 = C_2H_5AsI_2 + 2HgI + H_2.$$
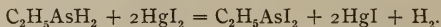
Stannic Chloride.—When 2.14 grams of ethylarsine (1 mol.) and 5.9 grams of stannic chloride (1 mol.) were sealed with ether in a tube, no solid formed even after standing for 14 months. No pressure was observed on opening the tube; the greenish yellow solution was concentrated and then treated with water; the aqueous solution contained the Sn″ ion and the oil separating was found to distil at 156° (ethylarsine dichloride boils at 156°).[2] The formation of the end products is explained by the equation

$$C_2H_5AsH_2 + 2SnCl_4 = C_2H_5AsCl_2 + 2SnCl_2 + 2HCl,$$
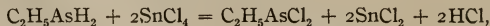
[1] See page 104, and cf. This Journal, **33**, 127; **35**, 35.
[2] La Coste: Ann. Chem. (Liebig), **208**, 33.

though evidence of intermediate products[1] was manifest in the oil separated.

Phosphorus Trichloride.—When equimolecular quantities of the two substances were brought together in an ether solution contained in a sealed tube, *a fine yellow powder* separated slowly. After 14 months the tube was opened; gaseous hydrochloric acid, ethylarsine dichloride, and a yellow orange solid were obtained. The residue persisted in giving off the odor of ethylarsine dichloride even though washed repeatedly with ether; the main ether solution, on being shaken with solid calcium chloride, gave a voluminous precipitate of a red brown substance. Evidently there was in solution some substance other than the *free* original compounds or the end product, ethylarsine dichloride.

Arsenic Trichloride.—When equimolecular quantities of the two substances were brought together in a sealed tube containing ether, *a yellow solid* appeared and changed rapidly to a curdy, *brick red* solid. Ethylarsine dichloride was found in the ether solution; the residue was analyzed for arsenic:

0.1387 gram substance gave 0.2214 gram $Mg_2As_2O_7$.

	Calculated for $(C_2H_5As)x$.	Found.
As	72.11	77.24

Evidently this residue is a mixture of the polymer $(C_2H_5As)_x$ with metallic arsenic and the equation representing the reaction is

$$8C_2H_5AsH_2 + 8AsCl_3 = (C_2H_5As)_4 + 4C_2H_5AsCl_2 + 16HCl + 8As.[2]$$
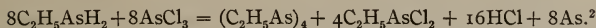
Antimony Trichloride.—When equimolecular quantities of the two substances were brought together in a sealed tube containing ether, *a red brown, amorphous solid* was formed immediately, but in the course of 14 months it changed to a *jet black solid*. Considerable pressure of gaseous hydrochloric acid was observed on opening the tube. The ether solution yielded ethylarsine dichloride and a little unchanged antimony trichloride; the black residue was washed repeatedly with ether but,

[1] Cf. This Journal, **35**, 39.
[2] Cf page 126.

on drying, *inflamed spontaneously.* Unquestionably intermediate products were formed in this experiment.

Water.—When 2 grams of ethylarsine and 5 grams of water were heated in a sealed tube for six hours at 180°, no evidence of a reaction could be observed.

Hydrochloric Acid Solution.—When ethylarsine was treated with an excess of one molecule of hydrochloric acid (sp. gr. 1.20) and the mixture was heated for two hours at 70°, no evidence of a reaction could be observed.

Isopropyl Iodide and Ethylarsine.—When 3.7 grams of ethylarsine and 18 grams of isopropyl iodide were heated to 70° for one hour in a sealed tube filled with carbon dioxide, no condensation was observed; after heating for three hours at 110°, a dark, red brown oil was obtained. The arsonium iodide (90 per cent) was separated in the usual manner; 0.2450 gram required 0.1155 gram of $AgNO_3$ = 35.22 per cent iodine; calculated, 35.18 per cent.

When a sample of 0.0546 gram of the *triisopropylethylarsonium iodide* was heated in the tensimeter molecular weight apparatus[1] the following data were obtained:

t.	Vapor pressure.	Vapor volume.	Apparent mol. wt.	Theoretical mol. wt.
130	0.0	0.0	. . . . .	360
179	1.2	0.007	. . . . .	. . .
198	8.3	0.044	. . . . .	. . .
234	388.3	2.066	411.6	. . .
240	1092.0	2.578	279.0	. . .
262	2138.0	3.428	146.5	. . .

The volume of nonreversible vapor at 28° was 2.7 cc.; it burned with a luminous flame, was free from arsenic and iodine, and was not affected by bromine water. On cooling, the residue, possessing an odor of tertiary arsine, consisted of a red yellow oil and light yellow crystals; the product reacted strongly with bromine water. Evidently triisopropylethylarsonium iodide *decomposes at its melting point,* according to the following reactions:

$$(C_3H_7)_3(C_2H_5)AsI = (C_3H_7)_3As + C_2H_5I,$$
$$2(C_3H_7)_3C_2H_5AsI = (C_3H_7)_3AsI_2 + C_4H_{10} + (C_3H_7)_3As.$$
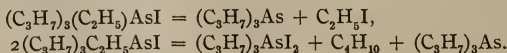
[1] J. Am. Chem. Soc., **29**, 1052.

n-Propyl Iodide and Ethylarsine.—When 2 grams of ethylarsine and 10 grams of *n*-propyl iodide were sealed in tubes filled with carbon dioxide and heated for one hour at 70°, no effect was observed; heated for three hours at 110°, much pressure (hydrogen) and a red oil were observed. *Tri-n-propylethylarsonium iodide* was separated and found to soften at 230° and melt at 237°, with decomposition. An alcoholic solution of the iodide treated with an alcoholic solution of mercuric iodide gave a light, yellow white precipitate, which, after recrystallizing from alcohol, gave, on analysis, 22.09 per cent of iodine; calculated for $(C_2H_5)(C_3H_7)_3AsHgI = 22.64$ per cent.[1]

Propylarsine.

n-Propylarsonic acid[2] (95 grams) and amalgamated zinc dust (500 grams) were placed in a flask and treated with concentrated hydrochloric acid, in the usual manner;[3] the *propylarsine* was condensed in a sulphur dioxide condenser surrounded by a freezing mixture. After transferring to bulbs of the proper size, it was analyzed:

0.1603 gram substance gave 0.1724 gram CO_2 and 0.1088 gram H_2O.

	Calculated for $C_3H_7AsH_2$.	Found.
C	7.50	7.54
H	30.00	29.33

Monobenzylarsine.

A 2-liter, hard glass, round bottom flask, containing 52 grams of benzylarsonic acid,[4] 200 cc. of ether, and 500 grams of amalgamated zinc dust[5] was connected with a reflux condenser, a dropping funnel, and a mercury valve; concentrated hydrochloric acid was dropped in until the reduction was complete:

$$C_6H_5CH_2AsO_3H_2 + 6H = C_6H_5CH_2AsH_2 + 3H_2O.$$

As the reduction proceeded, some red oxidation product was deposited upon the inner walls of the flask and a distinct odor

[1] Cf. Ann. Chem. (Liebig), **341**, 182.
[2] J. Am. Chem. Soc., **28**, 352.
[3] THIS JOURNAL, **33**, 120; **35**, 3.
[4] J. Am. Chem. Soc., **28**, 354. —should be 28,354
[5] THIS JOURNAL, **33**, 118.

of arsine was observed. After 2 to 3 days, more ether was added and the flask was shaken, then water was admitted through the dropping funnel until all of the ether solution (somewhat green in color) was forced up into a separatory funnel containing sticks of calcium chloride and filled with carbon dioxide. The separatory funnel was closed and shaken until the ether solution was dried. A Brühl distilling apparatus, properly connected with a condenser, a flask, and an inverted U-shaped delivery tube, was partially exhausted by means of the water pump; the delivery tube with proper connections was dipped to the bottom of the ether solution contained in the separatory funnel and the distilling flask was about half filled with the ether solution. By means of the pump, the ether solution was soon concentrated, then more of it was drawn in; this process was repeated until all of the ether solution had been evaporated at room temperature. The residual liquid, light yellow in color, was distilled, and the following fractions were obtained:

1.	140°	262	mm.	8.5	grams
2.	140°	260	"	4.1	"
3.	141°	260	"	3.2	"

The residue in the distilling flask changed finally and rather abruptly to a dark red solid. The apparatus was then filled with carbon dioxide and small bulbs, containing carbon dioxide, were filled with the different fractions:

0.1236 gram of fraction (1) gave 0.2260 gram CO_2 and 0.0602 gram H_2O.

	Calculated for $C_7H_9AsH_2$.	Found.
C	50.00	49.87
H	5.35	5.41

Benzylarsine is a faintly yellow liquid boiling at 140° under 262 mm. pressure.

Benzylarsine and Platinic Chloride.—When equimolecular weights of benzylarsine and platinic chloride (10 per cent solution) were brought together in a sealed tube, a black, oily substance, followed by a black amorphous mass, was noticed. After being washed with alcohol and ether, the *chlorplatinate*

was dried and ignited; the odors of arsenic trioxide and stibine were given off during the heating.

0.1121 gram substance yielded 0.0423 gram Pt.

	Calculated for $C_7H_7AsH_2.PtCl_4$.	Found.
Pt	38.49	38.18

Hydriodic Acid.—Heated with 2 molecules of hydriodic acid at 140° for one hour, the benzylarsine yielded hydrogen, a brown black solid,[1] and an oil (evidently benzylarsine diiodide).

Bromine.—With a molecule of bromine at ordinary temperature, the arsine yielded hydrogen, *transparent crystals*, and a heavy, dark oil.

Oxygen.—Permitted to oxidize in the air, the arsine yielded benzylarsonic acid (melting at 167°) and a red product, which was analyzed:

0.1180 gram substance gave 0.1837 gram $Mg_2As_2O_7$.

	Calculated for $(C_7H_7As)_4$.	Found.
As	76.72	75.33

Tripropylarsine.

When 103 grams of *n*-propyl chloride, 120 grams of arsenic trichloride, and 75 grams of sodium were brought together in a flask attached to a long reflux condenser, a reaction took place;[2] after standing all night and heating gently for 1 to 2 hours on the water bath, the reaction was found to be complete. After filtering rapidly and distilling off the ether, 60 grams of oil were obtained; this was distilled three times at ordinary pressure and the following fractions were obtained:

1.	100°–140°	2 grams	4.	205°–220°	10 grams
2.	140°–200°	8 "	5.	220°–270°	4 "
3.	200°–205°	18 "			

The lower fractions showed the presence of 2 to 3 per cent of chlorine; evidently primary and secondary arsine chlorides were present; on standing exposed to the air, a white solid formed and the oil separated into two layers; the solid gave, on

[1] See page 120.
[2] Cf. THIS JOURNAL, **35**, 42.

analysis, 4 per cent of chlorine; evidently the compound $(C_3H_7)_3$ $AsO.(C_3H_7)_2AsOCl$ was formed.

The fractions below 210° were boiled with an excess of bromine water; after concentrating, the heavy, red oil (25 grams) was washed with water, dried, and analyzed for bromine (21.42 per cent Br, calculated for $(C_3H_7)_2AsBr_2 = 43.90$ per cent). To remove the primary and secondary arsine derivatives which evidently were present, the oil was heated with aqueous ammonia and the residual oil was removed, reduced by means of zinc and hydrochloric acid, extracted with ether, and distilled under reduced pressure. It boiled at 167° (90 mm.) and 158° (73 mm.).

0.1312 gram substance gave 0.2550 gram CO_2 and 0.1183 gram H_2O.

	Calculated for $(C_3H_7)_3As.$	Found.
C	52.94	53.02
H	9.95	10.02

A molecular weight determination by the Dehn method[1] was made: 0.2242 gram substance gave 12.99 cc. of vapor at 1564 mm. and above 251°. Vapor pressures: 92°—161 mm.; 143°—283 mm.; 195°—482 mm.; 212°—844 mm.; 251°—1564 mm.

	Calculated for $(C_3H_7)_3As.$	Found.
Mol. wt.	202	204

Oxygen.—When tripropylarsine was brought into contact with air contained in the Dehn hygrometer,[2] no change in volume was observed; when a little concentrated sulphuric acid was then admitted, rapid oxidation resulted, as was shown by the rapid decrease of the air volume.

Decomposition of Arsenic Derivatives by Heat.[3]

Isoamylarsonic Acid.[4]—When 7.2 grams of the pure acid were heated in a sealed tube filled with carbon dioxide, no reaction was noticeable even after heating for 15 hours at 180° (the acid

[1] J. Am. Chem. Soc., **29**, 1063.
[2] *Ibid.*, **29**, 1053.
[3] Cf. J. Am. Chem. Soc., **28**, 355–59; This Journal, **35**, 8.
[4] J. Am. Chem. Soc., **28**, 353.

melts at 194°). After heating for three hours at 240°, a slight darkening and a partial yield of a liquid were observed; after heating for four hours at 285°, the formation of the liquid and a mass of pearly crystals was complete. On opening the tube, no pressure was observed; on distilling the liquid contents, a large yield of isoamyl alcohol and some isoamyl oxide was obtained. Since the flat, pearly crystals did not melt at 300°, did not suffer a loss in weight on subliming, and when dissolved in hydrochloric acid yielded with hydrogen sulphide a yellow precipitate, they were identified as arsenic trioxide. Therefore the above decomposition was as follows:

$$2C_5H_{11}AsO_3H_2 = 2C_5H_{11}OH + As_2O_3 + H_2O.$$
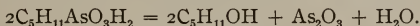
Phenylarsonic Acid.[1]—This acid did not decompose on heating for three hours at 285° (melting point, 158°); after heating for twenty-four hours at 320° it was changed to two liquid layers and a white solid (arsenic trioxide). The upper, dark colored liquid layer was separated from the lower layer (water) and identified as phenyl oxide (boiling point, 252°), therefore we have the following reaction:

$$2C_6H_5AsO_3H_2 = (C_6H_5)_2O + As_2O_3 + 2H_2O.$$
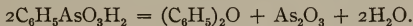
Monophenylarsine.[2]—When this compound was sealed in a tube with carbon dioxide and heated for two hours at 180°, no change was observed on cooling; after heating for three hours at 240°, a red brown solid and a light green oil were found; after heating for three hours more at 310°, a black residue coating the inner surfaces of the tube was observed. The excess of gas found in the tube proved to be hydrogen; an ether extract of the residue yielded well-defined crystals of triphenylarsine; the black residue contained 95.1 per cent of arsenic. Therefore the reaction is expressed by the following equation:

$$3C_6H_5AsH_2 = (C_6H_5)_3As + 2As + 3H_2.$$
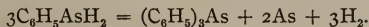
Monomethylarsine.[3]—This primary arsine was heated for three hours at 240° without effect; after heating for three

[1] Ann. Chem. (Liebig), **208**, 34; THIS JOURNAL, **33**, 132.
[2] THIS JOURNAL, **33**, 147.
[3] Ber. d. chem. Ges., **34**, 3597. THIS JOURNAL, **33**, 120.

hours at 310° it yielded a black, metallic mirror. The excess of gas formed was washed successively with solutions of sodium hydroxide, silver nitrate, and bromine; the residual gas, which burned with a blue flame, was proved by the explosion method to be a mixture of methane and hydrogen. At least one phase of the decomposition is expressed by the equation

$$2CH_3AsH_2 = 2CH_4 + 2As + H_2.$$

Monoethylarsine.[1]—When this arsine was heated for three hours at 210°, only a slight blackening was noticed; after three hours at 235°, the black metallic deposit on the walls of the tube was complete. The excess of gas in the tube was washed as described above. On exploding 0.9 of the residual gas in the presence of an excess of oxygen, it suffered a loss of 11.3 cc.; with potassium hydroxide a further loss of 8.4 cc. resulted. The black deposit (0.1036 gram) yielded 95.17 per cent of arsenic (0.1990 gram $Mg_2As_2O_7$). An alcohol-ether extract of the original contents of the tube yielded some triethylarsine. Therefore the following reactions are involved:

$$2C_2H_5AsH_2 = 2C_2H_6 + 2As + H_2,$$
$$3C_2H_5AsH_2 = (C_2H_5)_3As + 2As + 3H_2.$$
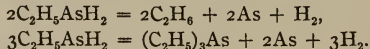
Diisoamylarsine.[2]—Heating for two hours at 220° yielded a little red solid; heating for three hours at 240° to 260° gave a black, metallic deposit. When 65 cc. of the excess gas were freed from carbon dioxide (22.2 cc.) and then was treated with bromine water, a contraction of 2.0 cc. resulted; the residual gas burned with a luminous flame. The liquid contents of the tube, after extracting with alcohol and ether, yielded at about 175° a liquid burning without depositing arsenic (decane) and at about 240° a liquid which, by its odor, by its decomposition on heating, and by its reaction with bromine, was proved to be *triisoamylarsine.* The black solid (0.1407 gram) gave on one analysis 86.48 per cent of arsenic (0.2466 gram $Mg_2As_2O_7$). The consecutive reactions probably are as follows:

$$6(C_5H_{11})_2AsH = 4(C_5H_{11})_3As + 2As + 3H_2,$$
$$2(C_5H_{11})_2AsH = C_5H_{10} + C_5H_{12} + C_{10}H_{22} + 2As.$$
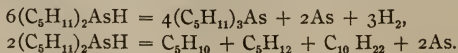
[1] THIS JOURNAL, **33**, 143.
[2] *Ibid.*, **35**, 53.

Diphenylarsine.[1]—Heating for two hours at 245° produced only a little blackening; heating for three hours at 295° effected decomposition. The residual excess gas proved to be hydrogen; the alcohol-ether extract of the residue yielded a white, crystalline product, which (0.0852 gram) yielded on analysis 25.15 per cent of arsenic (0.0443 gram $Mg_2As_2O_7$)—evidently it was triphenylarsine (calculated, As = 24.51 per cent). Two analyses of the black residue (77.46 per cent As and 77.70 per cent As) showed here, as in other cases of its production, that it is probably mixed with the tertiary arsine. The reactions are expressed by the following equations:

$$6(C_6H_5)_2AsH = 4(C_6H_5)_3As + 2As + 3H_2,$$
$$2(C_6H_5)_3As = 3C_{12}H_{10} + 2As.$$
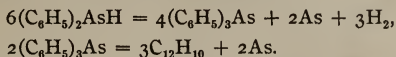
Tripropylarsine.[2]—No evidence of decomposition was noticeable below 287°; after heating for two hours at 295°, a yellow liquid was observed. On opening the tube considerable pressure was noticed; 44 cc. of this gas, after washing successively with caustic soda and bromine water, gave 16 cc. of gas which by shaking with alcohol lost 8.5 cc. The gas which was soluble in alcohol burned with a blue flame. The residual liquid in the tube had a cacodyllike odor. The probable partial reaction was

$$4(C_3H_7)_3As = (C_3H_7As)_4 + 4C_6H_{14}.$$

Triethylarsine.—Heated at 190° to 215° for three hours, it darkened; at 245° for two hours, a yellow oil and some solid were formed; at 265° for three hours, considerable excess gas, a greenish yellow to gray black residue and only a little liquid were observed. The solid gave, on analysis, 44.09 per cent arsenic (0.1264 gram gave 0.1129 gram $Mg_2As_2O_7$); calculated for $(C_2H_5)_3As = 46.29$. The alcohol-ether extract of the solid yielded an oil which by its odor and reaction with bromine was shown to be unchanged triethylarsine. The probable partial reaction was

$$4(C_2H_5)_3As = (C_2H_5As)_4 + 4C_4H_{10}.$$

[1] This Journal, **35**, 45.
[2] See page 115.

Benzylarsine.[1]—When 0.5 gram of benzylarsine, in a sealed tube from which the air had been exhausted, was heated for two hours at 250°, a reaction resulted. A little gas, a little oil, and a glistening, black solid were formed. The black solid was washed and analyzed; 0.1473 gram gave 0.1370 gram $Mg_2As_2O_7$, which is equivalent to 45.00 per cent of arsenic—calculated for $(C_6H_5CH_2As)_4$ is 45.18 per cent. Therefore the following reaction probably takes place:

$$4C_6H_5CH_2AsH_2 \rightarrow (C_6H_5CH_2As)_4 + 4H_2.$$
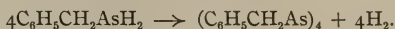
Cacodyl.[2]—When 5.3 grams of crude cacodyl (cacodylic oxide) were heated for two hours at 340° in a sealed tube filled with carbon dioxide, a black, metallic deposit and a mobile, yellow oil were formed; on opening the tube considerable pressure was observed. After washing with a solution of potash, the residual gas (about 25 per cent) was found to burn with an arsenic flame and to dissolve in a solution of silver nitrate; its odor and other properties characterized it as trimethylarsine.[3] After freeing it from the oil and washing it with alcohol and ether, 0.1446 gram of the black residue yielded 0.2500 gram $Mg_2As_2O_7$ or 83.65 per cent As; calculated for $(CH_3As)_4$ is 83.33 per cent As. The oil distilled mostly below 80° (trimethylarsine boils at 70°).[4] The decomposition of cacodyl at high temperatures is represented by the following equation:

$$4(CH_3)_2AsAs(CH_3)_2 \rightarrow 4(CH_3)_3 As + (CH_3As)_4.$$

That the oil was trimethylarsine was confirmed by the following experiments. Treated with an excess of an aqueous solution of mercuric chloride, a voluminous white precipitate was formed; by recrystallization from hot water, pearly white leaflets were obtained. 0.7070 gram substance gave 0.3918 gram AgCl.

	Calculated for $[(CH_3)_3As]_2HgCl_2$.	Found.
Cl	13.86	13.68

Trimethylarsine-mercuric chloride was formed.

[1] See page 113.
[2] Ann. Chem. (Liebig), **107**, 261. THIS JOURNAL, **35**, 2.
[3] Ann. Chem. (Liebig), **92**, 361; **112**, 228.
[4] Jahres. d. Chem., **1855**, 538.

A chloroform solution of trimethylarsine, treated with a chloroform solution of bromine, evolved much heat and precipitated a heavy, red oil that soon solidified to coarse, red orange, prismatic crystals. The substance was rapidly decomposed by atmospheric moisture and melted at 94°.

0.7088 gram substance gave 0.9481 gram AgBr.

	Calculated for $(CH_3)_3AsBr_2$.	Found.
Br	57.14	56.92

Trimethylarsine dibromide was formed.

III. Reactions of Dimethylarsine.[1]

With Burton B. Wilcox.

Isoamylene.—When equimolecular quantities of dimethylarsine and isoamylene were heated for one hour at 120°, no change was noticeable. Evidently a reaction indicated in the equation

$$(CH_3)_2AsH + C_5H_{10} = (CH_3)_2(C_5H_{11})As$$
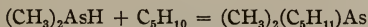
does not take place. The vapor pressures of amylene, methylarsine dichloride, and a mixture of the two in equal volumes were determined; these and other data are given below:

Temperature.	Isoamylene.	CH_3AsCl_2.	Mixture.	Vapor pressure depression.[2]
26.5	531.7	9.0	262.4	260.3
	Amyl chloride.	$AsCl_3$.		
28.5	64.3	11.0	54.9	20.6
	Propyl iodide.	$AsCl_3$.		
28.5	50.1	11.0	24.1	37.0

Benzyl Chloride.—Equimolecular quantities of dimethylarsine and benzyl chloride in ether solution in a sealed tube

[1] Secondary Arsines. Dehn and Wilcox: This Journal, **35**, 1–54.
[2] If the depression of vapor pressures of liquid mixtures is an indication of molecular coalescence, then the products

$$(CH_3)_2AsH \qquad Cl_3As \qquad Cl_3As$$
$$CH_2=CH-C_3H_7' \qquad Cl-C_5H_{11}' \qquad I-C_3H_7'$$
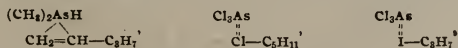
are probably formed, though the molecularly rearranged products

$$(CH_3)_2As-CH_2-CH_2-C_3H_7, \quad Cl_4As-C_5H_{11}, \quad Cl_3IAs-C_3H_7,$$
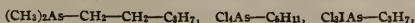
are not formed.

showed no evidence of reaction, after standing for two months.

Phosphoric Acid.—Equimolecular quantities of dimethylarsine and metaphosphoric acid in a sealed tube showed no evidence of reaction, even after heating for two hours at 95°.

Phenylarsine Dichloride.—When 2.06 grams of dimethylarsine (2 mols.) and 4.3 grams of phenylarsine dichloride (1 mol.) were brought together in a sealed tube filled with carbon dioxide, a dark, red brown solid and *fine, glistening crystals* were formed. Little pressure was observed on opening the tube (absence of hydrogen or hydrochloric acid gas); an ether extract of the contents of the tube, on being filtered and concentrated in a vacuum desiccator, yielded *beautiful, white, compact crystals*, which were immediately decomposed by atmospheric moisture. After washing with a little carbon disulphide, the crystals were dried and quickly analyzed for chlorine. 0.3683 gram of substance gave 0.3058 gram of AgCl.

	Calculated for $(C_6H_5AsCl_2)(CH_3)_2AsH$.	Found.
Cl	21.59	20.57

Dimethylarsinephenylarsine dichloride decomposes rapidly when exposed to the air, precipitating from an ether solution an oil, which was analyzed. 0.2514 gram substance gave 0.1641 gram AgCl.

	Calculated for $C_6H_5AsCl—As(CH_3)_2$.	Found.
Cl	12.00	16.62

The oil was evidently a mixture. The initial reaction of phenylarsine dichloride and dimethylarsine may be expressed thus:
$$\begin{array}{c} (CH_3)_2AsH \\ \| \\ C_6H_5—AsCl_2 \end{array}.$$
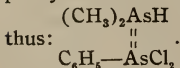
Diisoamylarsine Chloride.[1]—When equimolecular quantities of dimethylarsine and diisoamylarsine chloride were brought together in a sealed tube filled with carbon dioxide, no change was apparent to the eye, even after heating for five hours at 100°. On opening the tube no pressure (absence of dimethylarsine) was observed; after treating with water, the oil fumed,

[1] Cf. This Journal, **35**, 31.

possessed the odor of amylarsine, and undoubtedly was *diisoamyldimethylcacodyl*. The reaction evidently was as follows:

$$\begin{array}{ccc} (CH_3)_2AsH & & (CH_3)_2As \\ {}_{\parallel} & \longrightarrow & {}_{\mid} \quad + HCl. \\ (C_5H_{11})_2AsCl & & (C_5H_{11})_2As \end{array}$$
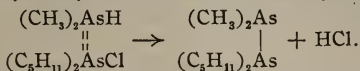
Propyl Iodide.—When 1.84 grams of dimethylarsine (1 mol.) and 5.83 grams of propyl iodide (2 mols.) were brought together in a sealed tube filled with carbon dioxide and the mixture was allowed to stand for a number of days, a slightly colored oil and some white crystals were formed. On opening the tube, pressure was observed; the crystals, easily decomposed by atmospheric moisture and forming an oil of a tertiary arsine odor, were nearly insoluble in chloroform (all tetralkylarsonium iodides are easily soluble in chloroform). After washing with chloroform they were analyzed with the following results: 0.9038 gram substance gave 0.7651 gram AgI.

	Calculated for $(CH_3)_2(C_3H_7)AsHI$.	Found.
I	46.01	45.75

Some of this *dimethyl-n-propylarsonium iodide* was treated with an excess of isoamyl iodide and heated in a sealed tube for two hours at 120°. The *dimethyl-n-propylisoamylarsonium iodide* was separated by the usual method:

0.6805 gram substance gave 0.4663 gram AgI.

	Calculated for $(CH_3)_2(C_3H_7)(C_5H_{11})AsI$.	Found.
I	36.70	37.03

Diisoamylarsine and n-Propyl Iodide. When 2.5 grams of diisoamylarsine (1 mol.) and 2.8 grams of *n*-propyl iodide (2 mols.) were heated for two hours at 160° in a sealed tube filled with carbon dioxide, a dark red liquid was obtained. On opening the tube, considerable gas was given off; after washing with caustic potash, alcohol, and water, the residual gas gave an excellent test for hydrogen. The product, *diisoamyldi-n-propylarsonium iodide*, was separated in the usual manner and analyzed with the following results: 0.6909 gram substance gave 0.3761 gram AgI.

	Calculated for $(C_5H_{11})_2(C_3H_7)_2AsI$.	Found.
I	29.53	29.42

Cacodyl and Propyl Iodide.—When 4.1 grams of crude cacodyl (1 mol.) and 12.5 grams of *n*-propyl iodide (4 mols.) were heated for 2 hours at 140° in a sealed tube filled with carbon dioxide, a red oil was obtained. After heating with a concentrated solution of potash, filtering, dissolving in chloroform, and reprecipitating with ether, the substance was obtained as yellow crystals. The process of purification was repeated 2 or 3 times but a colorless product could not be separated; after dissolving in a little water, filtering, and evaporating to dryness, light yellow crystals were obtained. 0.6882 gram substance gave 0.4980 gram AgI.

	Calculated for $(CH_3)_2(C_3H_7)_2AsI$.	Found.
I	39.93	39.11

When *dimethyldi-n-propylarsonium iodide* was treated with an excess of mercuric chloride, a white precipitate was formed; after crystallizing from hot water, white leaflets were obtained; 0.2960 gram substance gave 0.2556 gram AgI.2AgCl.

	Calculated for $(CH_3)_2(C_3H_7)_2AsIHgCl_2$.	Found.
I.2Cl	33.59	32.74

Acetyl Iodide and Dimethylarsine.—When equimolecular quantities of acetyl iodide and dimethylarsine were brought together in ether in a sealed tube, an immediate precipitation of a yellow solid and the liberation of considerable heat were observed. After some time the solid changed to a yellow oil and clusters of *needlelike crystals.* After two years, the tube was opened; the ether solution was treated with an aqueous solution of mercuric chloride, when a voluminous white precipitate was formed. After washing with water, alcohol, and ether the substance was analyzed. 0.3803 gram substance gave 0.2756 gram silver halide.

	Calculated for $(CH_3)_2AsH_4O.HgICl$.	Found.
Cl.I	33.51	31.10

The residue in the tube was washed repeatedly with ether and was then dissolved in water and boiled with a solution of mercuric chloride. The odor of acetaldehyde was observed,

while the oil, which was first formed, was slowly changed to mercurous iodide and the double compound with mercuric chloride. The reactions evidently can be represented as follows:

$$(CH_3)_2AsH \longrightarrow (CH_3)_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3C=O}{|}}{As}}{-}I \longrightarrow (CH_3)_2AsI + CH_3CHO.$$
$$CH_3CO{-}\overset{\shortparallel}{I}$$
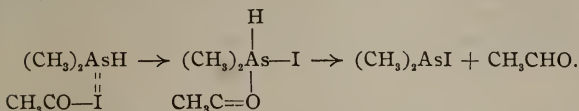
Chlorcarbonic Ethyl Ester and Dimethylarsine. When equimolecular quantities of the two substances were brought together in a sealed tube filled with carbon dioxide, no reaction was evident to the eye; however, on opening the tube, great pressure (ethyl formic ester boils at 54.4°) and combustible vapors were observed; the residual oil possessed the odor of cacodyl chloride, therefore a reaction had resulted, as follows:

$$(CH_3)_2AsH + ClCOOC_2H_5 \longrightarrow (CH_3)_2AsCl + HCOOC_2H_5.$$
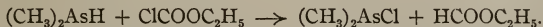
The oil was further identified as cacodyl chloride by shaking its ether solution with an aqueous solution of mercuric chloride —a voluminous white precipitate resulted. The substance was recrystallized from hot water. 0.5451 gram substance yielded 0.3970 gram AgCl.

	Calculated for $(CH_3)_2AsH_2O.HgCl_2$[1].	Found.
Cl	17.98	18.07

Sulphur Dichloride.[2] When 2.13 grams of dimethylarsine (2 mols.) and 2.06 grams of sulphur dichloride (1 mol.) were brought together in a sealed tube containing carbon dioxide, a very violent reaction (much heat) resulted. After standing for two years, a slightly yellow oil, a yellow amorphous solid (sulphur), and *transparent tablets and needles* were observed. On opening the tube a considerable pressure of methyl sulphide (identified by its odor and by the blackening of lead acetate paper) was observed. By heating the tube on the water bath, the liquid distilled out and the crystals increased in quantity (they did not melt at 100°). When treated with ether (evi-

[1] Cf. page 127.
[2] Cf. This Journal, **35**, 38.

dently containing a little water) the crystals were decomposed, thereby giving rise to the odor of cacodyl chloride and precipitating finely divided sulphur. A chloroform solution of the crystals standing in a desiccator deposited sulphur. These crystals were not analyzed; that they are an *intermediate* product in the following reaction is sufficiently evident:

$$2(CH_3)_2AsH + SCl_2 \longrightarrow 2(CH_3)_2AsCl + S.$$
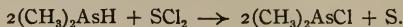
Arsenic Trioxide.—When 1.7 grams of dimethylarsine (3 mols.) and 2.1 grams of arsenic trioxide (2 mols.) were brought together in a sealed tube filled with carbon dioxide, a very slow reaction ensued—a dark brown solid gradually replaced the trioxide. The tube was heated for five hours at 100° and then was permitted to stand for two years; on opening the tube some unchanged arsine but no arsenic trioxide was observed. The red brown solid was analyzed.

0.1246 gram substance gave 0.2137 gram $Mg_2As_2O_7$.
0.1046 gram substance gave 0.1790 gram $Mg_2As_2O_7$.

	Calculated for		Found.	
	$As_2O_3(CH_3As)_4$.	$(CH_3As)_4$.	I.	II.
As	75.75	83.33	82.99	82.80

Evidently the reaction is largely as follows:

$$2(CH_3)_2AsH + As_2O_3 = (CH_3As)_4 + H_2O + O_2.$$
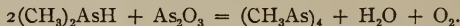
Arsenic Trichloride.[1]—When 3 grams of dimethylarsine (2 mols.) and 2.56 grams of arsenic trichloride (1 mol.) were brought together in ether in a sealed tube, a dark brown solid was precipitated at once. After standing for two years the ether solution was poured out; the amorphous brown solid was seen to be mixed with *long, prismatic, transparent crystals*, which were decomposed rapidly by contact with the atmosphere, hence they were not separated and analyzed. Evidently they were an *intermediate compound.* The red brown substance was washed with dilute hydrochloric acid and analyzed:

0.2453 gram substance gave 0.4238 gram $Mg_2As_2O_7$.

	Calculated for $(CH_3As)_4$.	Found.
As	83.33	83.60

[1] Cf. This Journal, **35**, 40.

The ether solution was treated with an aqueous solution of mercuric chloride; the voluminous white precipitate was recrystallized from hot water and analyzed.

0.6630 gram substance gave 0.4800 gram AgCl.

	Calculated for $(CH_3)_2AsH_2OHgCl_2$[1].	Found.
Cl	17.98	17.87

Evidently the end reaction is as follows:

$$4(CH_3)_2AsH + 2AsCl_3 = (CH_3As)_4 + 2(CH_3)_2AsCl + 4HCl$$
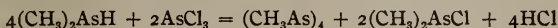
Urbana, Illinois,
August 5, 1907.

REVIEWS.

A Text-Book of Organic Chemistry. By A. F. Holleman, Ph.D., F. R. A. Amst., Professor Ordinarius in the University of Amsterdam. Translated from the Third Dutch Edition by A. Jamieson Walker, Ph.D. (Heidelberg), B. A., Head of the Department of Chemistry, Technical College, Derby, England. Assisted by Owen E. Mott, Ph.D. (Heidelberg). Second English Edition, Rewritten. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1907. Price, $2.50.

The author states that he has rewritten the chapter on pyrrol and that instead of giving prominence to any one formula for benzene he has presented the formulae of Kekulé, von Baeyer, and Thiele side by side. The treatment is otherwise similar to that in former editions.

The reviewer welcomes the use, in this book, of physical-chemical theories in the explanation of organic reactions. Such a large mass of facts connected with catalysis, tautomerism, and alkylation reactions is now known that there is a real demand for a text on physico-organic chemistry.

This new edition should receive the hearty reception given the former ones. S. F. Acree.

[1] Bunsen (Ann. Chem. (Liebig), **37**, 50) prepared from cacodylic oxide and mercuric chloride a white crystalline compound that seems to be identical with the above described substance, prepared from cacodyl chloride and mercuric chloride. Bunsen's analytical data agree more closely with the formula $(CH_3)_2AsHgCl.H_2O$ than with $[(CH_3)_2As]_2O.2HgCl$, which he assigned to the compound.

	Found. Bunsen	Calculated for		
		$(CH_3)_2AsHgCl_2.H_2O$.	$(CH_3)_2AsO.HgCl_2$.	$[(CH_3)_2AsH]_2O.2HgCl_2$
C	6.23	6.09	6.12	6.25
H	1.76	2.03	1.54	1.56
As	19.25	19.04	19.14	19.54
O	3.94	4.06	4.08	2.08
Hg	50.80	50.79	51.04	52.11
Cl	18.02	17.98	18.07	18.45

ORGANIC CHEMISTRY, Including Certain Portions of Physical Chemistry, for Medical, Pharmaceutical, and Biological Students (With Practical Exercises). By H. D. HASKINS, A.B., M.D., Instructor in Organic and Biochemistry, Medical Department, Western Reserve University, and Professor of Chemistry, Cleveland School of Pharmacy, and J. J. MacLEOD, M.B. (Aberd.), D.PH. (Camb.), Professor of Physiology, Western Reserve University. First Edition. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1907. Price, $2.

The authors state in the preface that this little book is written to present to biochemical students an outline of that part of organic chemistry which is most useful to them and to acquaint them with the physical-chemical conceptions and methods which are now of great importance. The text contains a large number of well selected experiments, and there are some useful tables at the end. An excellent feature of the book is the presentation of the graphical formulae of the important compounds in the sugar, alkaloid, and other groups.   S. F. ACREE.

EXERCISES IN ELEMENTARY QUANTITATIVE CHEMICAL ANALYSIS FOR STUDENTS OF AGRICULTURE. By AZARIAH THOMAS LINCOLN, PH.D., and JAMES HENRI WALTON, JR., PH.D., Assistant Professor of Chemistry, University of Wisconsin. New York: The Macmillan Co. 1907. pp. xv + 218. Price, $1.25.

This excellent manual presents a series of exercises designed particularly for the student of agriculture, by means of which he is taught the fundamental methods of quantitative chemical analysis as applied to a considerable range of inorganic substances of common occurrence and to those operations which are more directly typical of agricultural analysis. Representative procedures of gravimetric and volumetric analysis are included under the former category, and the methods for the analysis of milk, butter, cereals, fertilizers, and soils under the latter. A carefully written chapter on Stoichiometry follows, and the appendix contains a variety of useful information and a series of tables.

Under the plan adopted throughout the book, the procedures are given in considerable detail, and are followed by a series of explanatory notes, and references, to works of larger scope, or to articles in the journals which bear upon the methods described. With the usual allowance for necessary differences of opinion regarding the selection of a particular procedure, or the relative emphasis to be placed on a particular point, the manual appears to be worthy of hearty commendation. The typography is excellent and the text shows evidence of careful preparation.   H. P. TALBOT.

TRAITÉ COMPLET D'ANALYSE CHIMIQUE APPLIQUÉE AUX ESSAIS INDUS-
TRIELS. Par J. POST et B. NEUMANN. Deuxième édition française
entierement refondue. Traduite d'après la troisième édition alle-
mande et augmentée de nombreuses additions par le DR. L. GAUTIER
Tome second, premier fascicule. Paris: Librairie Scientifique A.
Hermann. 1908. pp. 199. Price, Fr. 6.

This is a faithful reproduction of the German edition noted
in the title above. The additions consist chiefly of certain
specifications regarding cements taken from the Annales
des Ponts et Chaussées. The German edition has already
been noticed in THIS JOURNAL. H. P. TALBOT.

DAIRY LABORATORY GUIDE. By CHARLES W. MELICK, B.S.A., M.SC.,
Professor of Dairy Husbandry, Maryland Agricultural Experiment
Station. Illustrations, 52. New York : D. Van Nostrand Company.
1907. pp. 129. Price, $1.25.

As its name indicates this book is a guide for the dairy
laboratory and not for the laboratory of dairy chemistry. It
is brief and condensed in its presentation of the subject and
does not pretend to describe apparatus or to explain the princi-
ples of the processes considered. Its object is to give in system-
atic order the various operations of a dairy or creamery and
with them some of the simpler chemical and bacteriological
tests. The arrangement of the book is good and it is well
written and printed.

For the student under the direction of an instructor and in
a laboratory where the various forms of apparatus mentioned
are in use, it will serve as an aid in directing and systematiz-
ing the work. It cannot, however, be used with profit by any
one outside of a laboratory of instruction.

The book covers considerable ground and presents for study
the more common operations in the handling of milk and the
manufacture of milk products. It also contains sections deal-
ing with mechanical contrivances, repair of machinery, modi-
fied milk, standardized milk, condensed milk, refrigeration,
pasteurization and receipts for various materials made from
milk. There are a few misstatements and typographical errors,
but these are neither numerous nor serious in nature.

J. S. C.

MEMENTO DU CHIMISTE (ancien Agenda du Chimiste). Recueil de
tables et de documents divers indispensables aux laboratoires officiels
et industriels, publié sous la direction de A. HALLER, Membre de
l'Institut, et CH. GIRARD, Directeur du Laboratoire Municipal de
Paris. Paris: H. Dunod et E. Pinat. 1907. xx + 758 pp. Price,
Fr. 12.

This book marks the revival, under a somewhat modified
form, of the "Agenda du Chimiste" which appeared annually

from 1877 to 1897. It is similar in character to Biedermann's well-known "Chemiker Kalender," but is printed in larger and clearer type. The first 172 pages contain various mathematical and physical tables, 190 pages are given to analytical data and to the formulas and principal physical properties of inorganic and organic compounds and of minerals, and the balance of the book is devoted to information concerning applied and industrial chemistry. A portrait of Charles Friedel and a brief sketch of the life and work of this chemist are given in the introduction. Every laboratory worker will find this a very useful book to have on his table.   C. A. R.

AMERICAN

CHEMICAL JOURNAL

CLVII.—RESEARCHES ON PYRIMIDINES: THE ACTION OF POTASSIUM THIOCYANATE UPON SOME IMIDECHLORIDES.

[THIRTY-FIFTH PAPER.]

By Treat B. Johnson and Walter F. Storey.

Two papers entitled ''The Action of Potassium Thiocyanate upon Imidechlorides'' have previously been published from this laboratory.

In the first paper[1] the authors showed that the three imidechlorides, *viz.*, 2-ethylmercapto-6-chlorpyrimidine, I., 2-ethylmercapto-5-methyl-6-chlorpyrimidine, II., and 2-ethylmercapto-5-brom-6-chlorpyrimidine, III., reacted with potassium thiocyanate, under certain conditions, giving isothiocyanates. They made no attempts to obtain evidence of the intermediate formation of thiocyanates.

$$
\begin{array}{ccc}
N = CCl & N = CCl & N = CCl \\
| \quad | & | \quad | & | \quad | \\
C_2H_5SC \quad CH & C_2H_5SC \quad CCH_3 & C_2H_5SC \quad CBr. \\
\| \quad \| & \| \quad \| & \| \quad \| \\
N - CH & N - CH & N - CH \\
I. & II. & III.
\end{array}
$$
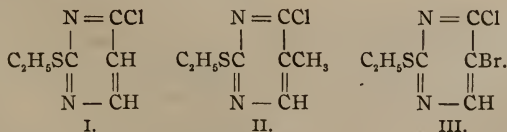
[1] Wheeler and Bristol: This Journal, **33**, 448.

In the second paper,[1] Johnson and McCollum described an unique case of the molecular rearrangement of a thiocyanate into an isothiocyanate. They observed that 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine, IV., reacted, in alcohol, with potassium thiocyanate, giving 2-ethylmercapto-5-ethoxy-6-thiocyanpyrimidine, V., which then underwent a metameric change into 2-ethylmercapto-5-ethoxy-6-isothiocyanpyrimidine, VI.

$$
\begin{array}{ccc}
\text{N}=\text{CCl} & \text{N}=\text{CSCN} & \text{N}=\text{CNCS} \\
| \quad | & | \quad | & | \quad | \\
\text{C}_2\text{H}_5\text{SC} \quad \text{COC}_2\text{H}_5 & \text{C}_2\text{H}_5\text{SC} \quad \text{COC}_2\text{H}_5 & \text{C}_2\text{H}_5\text{SC} \quad \text{COC}_2\text{H}_5. \\
\| \quad \| & \| \quad \| & \| \quad \| \\
\text{N}-\text{CH} & \text{N}-\text{CH} & \text{N}-\text{CH} \\
\text{IV.} & \text{V.} & \text{VI.}
\end{array}
$$
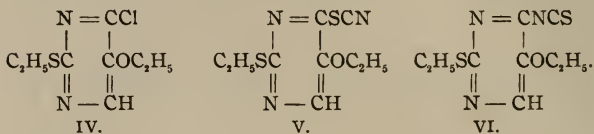
The work described in this paper was undertaken with the object of examining the behavior of potassium thiocyanate towards the three cyclic imidechlorides, *viz.*, 2-paratoluidino-6-chlorpyrimidine, VII., 2-orthotoluidino-6-chlorpyrimidine, VIII., and 2-paratolyl-4-methyl-6-chlorpyrimidine, IX. Incidentally we have also reinvestigated the action of potassium thiocyanate on the imidechlorides, I., II., and III., studied by Wheeler and Bristol.

$$
\begin{array}{cc}
\text{N}=\text{CCl} & \text{N}=\text{CCl} \\
| \quad | & | \quad | \\
p\text{-CH}_3.\text{C}_6\text{H}_4\text{NHC} \quad \text{CH} & o\text{-CH}_3.\text{C}_6\text{H}_4\text{NHC} \quad \text{CH} \\
\| \quad \| & \| \quad \| \\
\text{N}-\text{CH} & \text{N}-\text{CH} \\
\text{VII.} & \text{VIII.}
\end{array}
$$

$$
\begin{array}{c}
\text{N}=\text{CCl} \\
| \quad | \\
p\text{-CH}_3\text{C}_6\text{H}_4\text{C} \quad \text{CH.} \\
\| \quad \| \\
\text{N}-\text{CCH}_3 \\
\text{IX.}
\end{array}
$$
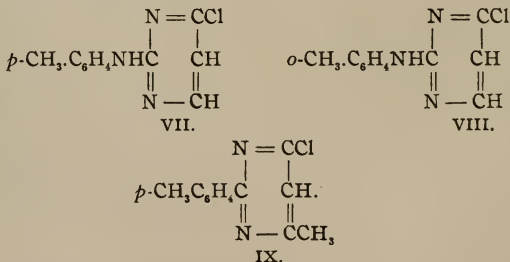
2-Paratoluidino-6-chlorpyrimidine, VII., and 2-orthotoluidino-6-chlorpyrimidine, VIII., were prepared from 2-ethylmercapto-6-oxypyrimidine. This mercaptopyrimidine reacted, in a smooth manner, with *para-* and *ortho*toluidine, at 100°, giving quantitative yields of 2-paratoluidino-6-oxypyrimidine

[1] This Journal, **36**, 136.

and 2-orthotoluidino-6-oxypyrimidine, respectively. The oxy-pyrimidines were then converted into the imidechlorides, VII. and VIII., by treatment with phosphorus oxychloride or phosphorus pentachloride. These two chlorides are more stable in alcoholic solutions than the corresponding 2-ethyl-mercapto-6-chlorpyrimidine. While the mercapto deriva-tive is decomposed by boiling alcohol the toluidinopyrimi-dines can be recrystallized repeatedly from this solvent with-out alteration. We now find that these two chlorides do not react with potassium thiocyanate under normal conditions. They were recovered unaltered after digesting, in alcohol or acetone, with potassium thiocyanate for several hours.

On the other hand, 2-paratolyl-4-methyl-6-chlorpyrimidine, IX., which was obtained from 2-paratolyl-4-methyl-6-oxy-pyrimidine[1] by the action of phosphorus pentachloride, re-acted in a smooth manner with potassium thiocyanate, giv-ing a good yield of 2-paratolyl-4-methyl-6-thiocyanpyrimi-dine, X. This thiocyanate was stable at ordinary tempera-ture and reacted with thiobenzoic acid, giving a quantitative yield of 2-paratolyl-4-methyl-6-thiopyrimidine. When heated above its melting point, the thiocyanate was converted into a mixture of the isothiocyanate, XI., and apparently a poly-meric form of the isothiocyanate melting at 204°. The iso-thiocyanate reacted with aqueous ammonia at ordinary tem-perature, giving 2-paratolyl-4-methyl-6-thioureapyrimidine, XII.

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{C} \begin{array}{c} \text{N} = \text{CSCN} \\ | \quad | \\ \text{CH} \\ || \quad || \\ \text{N} - \text{CCH}_3 \end{array}$$
X.

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{C} \begin{array}{c} \text{N} = \text{CNCS} \\ | \quad | \\ \text{CH} \\ || \quad || \\ \text{N} - \text{CCH}_3 \end{array}$$
XI.

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{C} = \begin{array}{c} \text{N} = \text{CNHCSNH}_2 \\ | \quad | \\ \text{CH}. \\ || \quad || \\ \text{N} - \text{CCH}_3 \end{array}$$
XII.
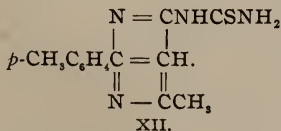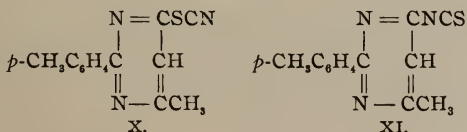
[1] Glock: Ber. d. chem. Ges., **21,** 2658.

Wheeler and Bristol,[1] in their investigation of the action of potassium thiocyanate on the imidechlorides, 2-ethylmercapto-6-chlorpyrimidine, I., 2-ethylmercapto-5-methyl-6-chlorpyrimidine, II., and 2-ethylmercapto-5-brom-6-chlorpyrimidine, III., worked with the object of converting these chlorides into isothiocyanates. They invariably digested the chlorides with potassium thiocyanate in toluene or alcohol for 3 to 15 hours. Under these conditions the thiocyanates, if formed, would be converted completely into isothiocyanates. We now find that these imidechlorides give practically quantitative yields of the thiocyanates XIII., XIV., and XV., when warmed in alcohol with potassium thiocyanate, if the time of digestion is limited to 20 to 60 minutes. The thiocyanates are stable at ordinary temperature and can be recrystallized from alcohol without alteration. They rearrange smoothly into isothiocyanates when heated above their melting points or when digested for long periods with alcohol. The isothiocyanates, when formed under the latter condition, react with the alcohol, giving the corresponding 6-thiourethanepyrimidines:

$$
\begin{array}{ccc}
\text{N == CSCN} & \text{N == CSCN} & \text{N == CSCN} \\
| \quad\quad | & | \quad\quad | & | \quad\quad | \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CH} & \text{C}_2\text{H}_5\text{SC} \quad \text{CCH}_3 & \text{C}_2\text{H}_5\text{SC} \quad \text{CBr.} \\
\| \quad\quad \| & \| \quad\quad \| & \| \quad\quad \| \\
\text{N --- CH} & \text{N --- CH} & \text{N --- CH} \\
\text{XIII.} & \text{XIV.} & \text{XV.}
\end{array}
$$
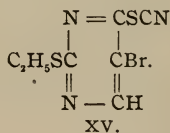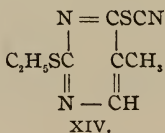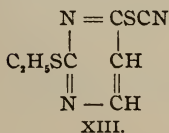
The melting points and boiling points of all the 6-thiocyanpyrimidines, 6-isothiocyanpyrimidines, and corresponding 6-thioureapyrimidines, which have been prepared in this laboratory, are given in the following table:

[1] *Loc. cit.*

6-Oxypyrimidines.	6-Chlorpyrimidines.	6-Thiocyanpyrimidines.	6-Isothiocyanpyrimidines.	6-Thioureapyrimidines.
C_2H_5SC — NH — CO[1] ‖ | N= CH | ‖ N —— CH m. 152°.	$C_6H_7N_2S(Cl)$.[2] b_{24} 135°.	$C_7H_7N_3S(SCN)$.[4] m. 82°.	$C_7H_7N_3S(NCS)$.[4] $b_{15.50}$ 200°-205°. $[C_7H_7N_3S(NCS)]_x$.[3] m. 175°.	$C_8H_{12}N_4S(NHCSNH_2)$.[3] m. 214°.
C_2H_5SC — NH — CO[2] ‖ | N= CCH₃ | ‖ N —— CH m. 159°.	$C_7H_9N_2S(Cl)$.[2] b_{25} 157°.	$C_8H_9N_3S(SCN)$.[4] m. 95°.	$C_8H_9N_3S(NCS)$.	$C_9H_{14}N_4S(NHCSNH_2)$.[3] m. 192°.
C_2H_5SC — NH — CO[2] ‖ | N= CBr | ‖ N —— CH m. 189°.	$C_6H_6N_2SBr(Cl)$.[3] b_{25} 168°.	$C_7H_6N_3SBr(SCN)$.[4] m. 81°-82°.	$C_7H_6N_3SBr(NCS)$.[4] m. 79°-80°.	$C_8H_{11}N_4SBr(NHCSNH_2)$.[3] m. 220°.
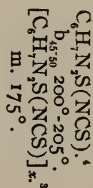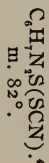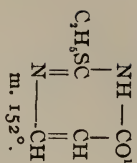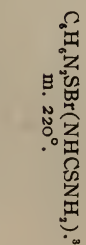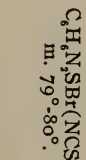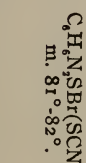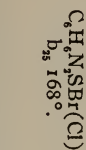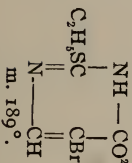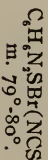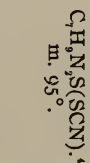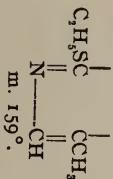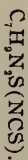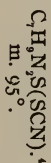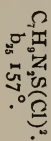
[1] Wheeler and Merriam: This Journal, **29**, 484.
[2] Wheeler and Johnson: *Ibid*, **29**, 492; **31**, 591.
[3] Wheeler and Bristol: *Ibid*, **33**, 448.
[4] This paper.

6-Oxypyrimidines.	6-Chlorpyrimidines.	6-Thiocyanpyrimidines.	6-Isothiocyanpyrimidines.	6-Thioureapyrimidines.
$\begin{array}{c} \text{NH—CO}[1] \\ C_7H_5SC \qquad COC_6H_5 \\ \text{N═══CH} \\ \text{m. }169°. \end{array}$	$C_9H_{11}ON_2S(Cl)$[1] b_{25} 185°. m. 46°.	$C_9H_{11}ON_2S(SCN)$[1] m. 66°-67°.	$C_9H_{11}ON_2S(NCS)$[1] m. 45°-50°.	$C_9H_{11}ON_2S(NHCSNH_2)$[1] m. 172°.
$\begin{array}{c} \text{NH—CO}[2] \\ p\text{-}CH_3C_6H_4C \qquad CH \qquad CCH_3 \\ \text{N═══CCH}_3 \\ \text{m. }216°. \end{array}$	$C_{12}H_{11}N_2(Cl)$[3] m. 107°.	$C_{12}H_{11}N_2(SCN)$[3] m. 123°.	$[C_{12}H_{11}N_2(NCS)]x$[3] m. 207°-208°.	$C_{12}H_{11}N_2(NHCSNH_2)$[3] m. 145°-146°.

[1] Johnson and McCollum: This Journal, **38**, 136; J. Biolog. Chem., **1**, 437.
[2] Loc. cit.
[3] This paper.

EXPERIMENTAL PART.

2-*Ethylmercapto-6-thiocyanpyrimidine*, $C_2H_5S.C$

$$
\begin{array}{cc}
N = CSCN \\
| \quad\quad | \\
C_2H_5S.C \quad CH \\
\| \quad\quad \| \\
N - CH
\end{array}
$$
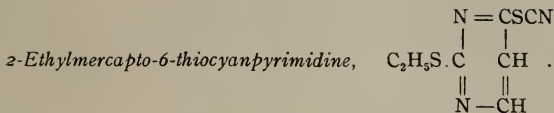
BY DR. E. V. McCOLLUM.

Three and nine-tenths grams of potassium thiocyanate were dissolved in 40 cc. of 95 per cent alcohol and 7 grams of 2-ethylmercapto-6-chlorpyrimidine added to the solution. There was an immediate reaction with separation of potassium chloride. The mixture was warmed on the steam bath for twenty minutes and the insoluble potassium chloride separated by filtration. On cooling the alcohol solution, the thiocyanate deposited in prismatic crystals which were purified for analysis by recrystallization from alcohol. It separated in aggregates of rectangular prisms melting without effervescence at 82° to a clear oil. The compound was insoluble in alkali and did not react with ammonia or aniline at 100°. Analysis (Kjeldahl):

		Found.	
Calculated for $C_7H_7N_3S_2$.	I.	II.	III.
N 21.31	20.89	21.32	21.09

When the alcohol filtrates were combined and evaporated to dryness a yellow, crystalline residue was obtained which partially dissolved in cold 10 per cent solution of sodium hydroxide. When this solution was acidified with acetic acid we obtained 0.3 gram of material which crystallized from alcohol in flat prisms or plates melting at 92°–93°. The compound was identical with the 2-ethylmercapto-6-thionethylurethanepyrimidine described by Wheeler and Bristol.[1] A quantitative yield of the above thiocyanate can be obtained by boiling 2-ethylmercapto-6-chlorpyrimidine in acetone solution with potassium thiocyanate. It was very soluble in acetone and separated in prismatic crystals melting at 81°–82°.

[1] *Loc. cit.*

$$\text{2-Ethylmercapto-6-isothiocyanpyrimidine,} \quad \begin{matrix} & N{=}C.NCS \\ & | \qquad | \\ C_2H_5SC & CH \\ & \| \quad \| \\ & N{-}CH \end{matrix} \ .$$
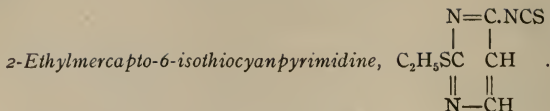
BY DR. E. V. McCOLLUM.

2-Ethylmercapto-6-thiocyanpyrimidine shows no tendency to rearrange to the isothiocyanate at ordinary temperature. On the other hand, a rearrangement took place when the thiocyanate was heated for 4 to 5 hours at 80°–90°. The isothiocyanate was obtained as an oil which reacted at once with aniline, giving 2-ethylmercapto-6-phenylthioureapyrimidine[1] melting at 205°.

The isothiocyanate was obtained as a yellow oil boiling at 200°–205° (45–50 mm.) when the thiocyanate was distilled. It did not crystallize on standing but a yellow, crystalline compound slowly deposited. This was difficultly soluble in benzene and practically insoluble in alcohol. It melted at 175°–177° and did not react with ammonia. The compound is apparently identical with the product which Wheeler and Bristol obtained by treating 2-ethylmercapto-6-chlorpyrimidine with potassium thiocyanate. It is probably a polymeric form of the isothiocyanate, $(C_7H_7N_3S_2)_x$.

The isothiocyanate reacted at once with aqueous ammonia, with evolution of heat, giving 2-ethylmercapto-6-thioureapyrimidine[2] melting at 214°.

2-Ethylmercapto-5-methyl-6-thiocyanpyrimidine,

$$\begin{matrix} & N{=}C.SCN \\ & | \qquad | \\ C_2H_5SC & CCH_3. \end{matrix}$$ —Five grams of 2-ethylmercapto-5-methyl-

$$\begin{matrix} \| \quad \| \\ N{-}CH \end{matrix}$$
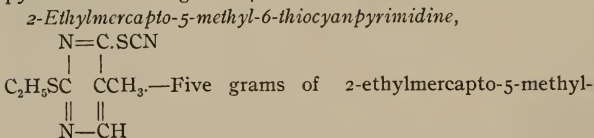
6-chlorpyrimidine and 3.5 grams of dry potassium thiocyanate were dissolved in 25 cc. of absolute alcohol and the solution boiled for 1 hour. The undissolved potassium chloride was then filtered off and the solution evaporated on the steam bath. We obtained a syrup which was triturated with cold water to remove any potassium chloride and then extracted

[1] Wheeler and Bristol: *Loc. cit.*
[2] *Ibid.*

with ether. When the ether was evaporated we obtained an oil which did not solidify after standing for several days. This oil partially dissolved in 10 per cent sodium hydroxide. The insoluble portion solidified on standing, and crystallized from 95 per cent alcohol in beautiful prisms melting without effervescence at 95° to a clear oil. It did not react with ammonia or aniline and a nitrogen determination agreed with the calculated value for a thiocyanate (Kjeldahl):

	Calculated for $C_8H_9N_3S_2$.	Found.
N	19.90	19.6

The thiocyanate dissolved at once in cold thioacetic acid without apparent evolution of heat. On standing, beautiful prismatic crystals deposited which melted at 179°–180°. This compound was not examined further but it probably was *2-ethylmercapto-5-methyl-6-thiopyrimidine*. It dissolved in alkalis and gave a test for sulphur.

When the sodium hydroxide solution (above) was acidified with acetic acid we obtained an oil which soon solidified. It was insoluble in water but crystallized from 95 per cent alcohol in stout prisms melting at 90°. It was identical with *2-ethylmercapto-5-methyl-6-thionurethanepyrimidine*,

$$\begin{array}{c} N{=}C.\,NHCSOC_2H_5 \\ |\qquad | \\ C_2H_5SC\quad CCH_3 \\ \|\qquad \| \\ N{-}CH \end{array}$$

, which was described by Wheeler and Bristol.[1] A mixture of the two compounds melted at 89°–90°.

2-Ethylmercapto-5-brom-6-thiocyanpyrimidine,

$$\begin{array}{c} N = CSCN \\ |\qquad | \\ C_2H_5S.C\quad CBr. \\ \|\qquad \| \\ N - CH \end{array}$$

—This thiocyanate was prepared in the following manner: Five grams of 2-ethylmercapto-5-brom-6-chlorpyrimidine and 2.5 grams of potassium thiocyanate were dissolved in 50 cc. of 95 per cent alcohol and the solution boiled on the steam bath for 20 minutes. The insoluble potassium

[1] *Loc. cit.*

chloride was filtered off and the filtrate cooled, when the thiocyanate deposited in prisms melting at 81°–82°. They were very soluble in acetone, boiling ligroin, warm alcohol, and benzene. The compound did not dissolve in sodium hydroxide and could be warmed with ammonia without alteration. Analysis (Kjeldahl):

	Calculated for $C_7H_6N_3S_2Br$.	I.	II.
			Found.
N	15.21	15.32	15.28

Action of Thioacetic And Thiobenzoic Acids On 2-Ethyl-mercapto-5-brom-6-thiocyanpyrimidine:—About 0.3 gram of the thiocyanate was dissolved in a small quantity of thioacetic acid. Reaction took place at once, on warming, without evolution of carbon bisulphide, giving large, well-developed prisms. The compound crystallized from benzene in rhombic prisms that melted at 198° with slight effervescence. It was identified as 2-ethylmercapto-5-brom-6-thiopyrimidine.[1] A mixture of the two products melted at the same temperature. The same 6-thiopyrimidine was obtained when the thiocyanate was warmed in a water bath with a molecular proportion of thiobenzoic acid.

Rearrangement of 2-Ethylmercapto-5-brom-6-thiocyanpyrimidine into the Isothiocyanate:—About 0.2 gram of the thiocyanate was heated for 2 hours at 150°–160°. We obtained a red oil which solidified on cooling and melted at 75°–80°. That a rearrangement had taken place was shown in the following manner: The compound (melting at 75°–80°) reacted at once with ammonia, giving 2-ethylmercapto-5-brom-6-thiourea-pyrimidine[2] melting at 219°–220°. A mixture of the two preparations melted at the same temperature.

2-Orthotoluidino-6-oxypyrimidine, o-CH₃.C₆H₄NH.C

$$\begin{array}{c} NH-CO \\ | \quad\quad | \\ o\text{-}CH_3.C_6H_4NH.C \quad CH.- \\ || \quad\quad || \\ N -.CH \end{array}$$

Eighteen grams of 2-ethylmercapto-6-oxypyrimidine and one molecular proportion of orthotoluidine (14 grams) were heated together on the steam bath for 3 days. The evolution of

[1] Wheeler and Bristol: *Loc. cit.*

[2] *Ibid.*

mercaptan was then complete and a compound was obtained which was difficultly soluble in alcohol. It crystallized from hot alcohol or acetic acid in prismatic crystals melting at 219°–220°. It was soluble in alkali. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found.	
		I.	II.
N	20.89	20.93	20.74

$$N = CCl$$
2-Orthotoluidino-6-chlorpyrimidine, $o\text{-}CH_3.C_6H_4NH.C$ CH.
$$N — CH$$
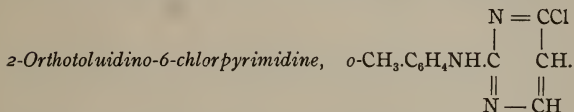
—Ten grams of 2-orthotoluidino-6-oxypyrimidine were heated on the steam bath with 25 cc. of phosphorus oxychloride until the evolution of hydrochloric acid gas ceased. The excess of phosphorus oxychloride was then distilled under diminished pressure. We obtained a yellow oil, which assumed a crystalline form when treated with ammonia. The compound crystallized from alcohol in corpuscular crystals melting at 78°. It was insoluble in alkali. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}N_3Cl$.	Found.	
		I.	II.
N	19.1	18.8	18.92

Action of Potassium Thiocyanate on 2-Orthotoluidino-6-chlorpyrimidine:—Four grams of the chlorpyrimidine and 3 grams of potassium thiocyanate were dissolved in 50 cc. of alcohol and the solution boiled for 2 hours. After filtering a small amount of insoluble material the excess of alcohol was evaporated on the steam bath. We obtained a crystalline residue which crystallized from alcohol and melted at 77°–78°. It responded to a test for chlorine and was identified as the unaltered chloride. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}N_3Cl$.	Found.
N	19.1	19.07

2-Orthotoluidino-6-aminopyrimidine,
$$N = CNH_2$$
$o\text{-}CH_3.C_6H_4NHC$ CH. — 2-Orthotoluidino-6-chlorpyrimidine
$$N — CH$$
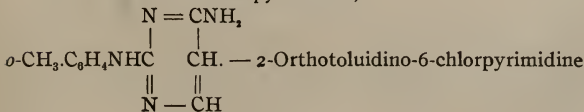
does not react with ammonia at ordinary temperature. When heated with alcoholic ammonia for 2 hours at 140°–150° it gave a quantitative yield of the aminopyrimidine. This was very soluble in alcohol and crystallized from dilute alcohol in aggregates of small prisms melting at 124°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{12}N_4$.	Found.
N	28.00	27.7

2-Orthotoluidino-6-anilinopyrimidine,
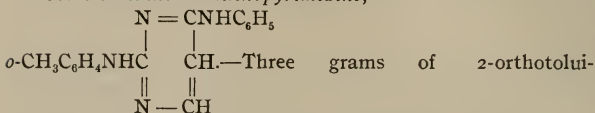
$$\begin{array}{c} N = CNHC_6H_5 \\ | \quad | \\ o\text{-}CH_3C_6H_4NHC \quad CH. \\ || \quad || \\ N - CH \end{array}$$—Three   grams   of   2-orthotolui-

dino-6-chlorpyrimidine and 4 grams of aniline were dissolved in 25 cc. of benzene and the solution boiled for 6 hours. It was then filtered and evaporated to dryness. We obtained a crystalline residue which was washed with water to remove aniline hydrochloride and then dissolved in warm dilute hydrochloric acid. The hydrochloride of the anilinopyrimidine crystallized, on cooling, in slender needles melting at 126°. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4 \cdot HCl$.	Found.
N	17.92	17.73

When the hydrochloride was dissolved in water and ammonia added to the solution the free base separated. It crystallized from dilute alcohol in hexagonal plates melting at 128° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4$.	Found.
N	20.28	20.29

2-Paratoluidino-6-oxypyrimidine, $p\text{-}CH_3.C_6H_4NHC$ $$\begin{array}{c} NH - CO \\ | \quad | \\ CH. \\ || \quad || \\ N - CH \end{array}$$—
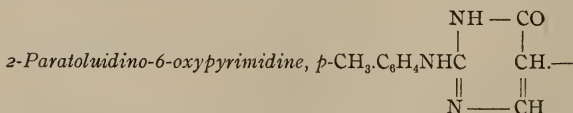
This compound is formed, in a smooth manner, by heating 2-ethylmercapto-6-oxyprimidine with a molecular proportion of paratoluidine at 100°. It was difficultly soluble in warm alcohol, acetone, boiling water, and cold acetic acid. It crystal-

lized from acetic acid in clusters of needles melting at 270°–271°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	21.0

2-*Paratoluidino-6-chlorpyrimidine,* p-CH$_3$C$_6$H$_4$NH.C $\begin{matrix} \text{N} == \text{CCl} \\ | \quad\quad | \\ \text{C} \quad\quad \text{CH} \\ || \quad\quad || \\ \text{N} — \text{CH} \end{matrix}$—
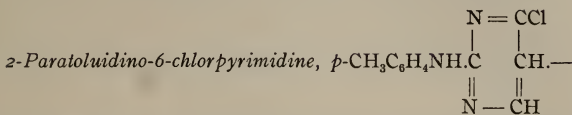
Twenty-six grams of 2-paratoluidino-6-oxypyrimidine were digested with 65 cc. of phosphorus oxychloride until the evolution of hydrochloric acid gas ceased. We obtained a dark colored solution which was heated at 100° under diminished pressure to remove the excess of phosphorus oxychloride. The residue was dissolved in ice water and the solution made alkaline with ammonia when the chlorpyrimidine deposited. It crystallized from alcohol in prisms melting at 112°–113° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}N_3Cl$.	Found.
N	19.13	18.99

Action of Potassium Thiocyanate on 2-Paratoluidino-6-chlorpyrimidine:—This pyrimidine was recovered unaltered, melting at 112°–113°, after warming, in acetone solution, with potassium thiocyanate for 2.5 hours.

2-*Paratoluidino-6-anilinopyrimidine,*

p-CH$_3$C$_6$H$_4$NHC $\begin{matrix} \text{N} == \text{CNHC}_6\text{H}_5 \\ | \quad\quad | \\ \text{C} \quad\quad \text{CH} \\ || \quad\quad || \\ \text{N} — \text{CH} \end{matrix}$—The hydrochloride of this base
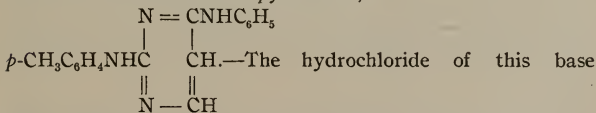
was obtained when 2-paratoluidino-6-chlorpyrimidine was warmed in benzene with aniline. The salt was very soluble in hot water and alcohol. It crystallized from alcohol in prisms which decomposed at 134°. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4$.HCl.	Found.
N	17.92	17.96

When sodium hydroxide was added to an aqueous solution of this salt the pyrimidine base deposited in needles. It was

insoluble in hot water, and crystallized from alcohol in needles melting at 135° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4$.	Found.
N	20.28	20.15

2-β-Naphthylamino-6-oxypyrimidine, β-$C_{10}H_7NH.C$

$$\begin{array}{cc} NH\!-\!CO \\ | \qquad | \\ C \quad CH.\!- \\ \| \qquad \| \\ N\!-\!-\!CH \end{array}$$
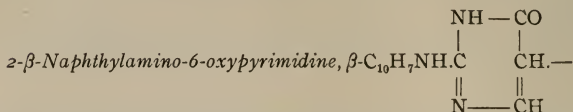
From β-naphtylamine and 2-ethylmercapto-6-oxypyrimidine. It was insoluble in hot water and difficultly soluble in alcohol. It crystallized from alcohol in clusters of needles melting at 270°. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{11}ON_3$.	Found.
N	17.72	17.77

2-Paratolyl-4-methyl-6-chlorpyrimidine,

p-$CH_3C_6H_4.C$
$$\begin{array}{cc} N = CCl \\ | \qquad | \\ CH.\!- \\ \| \qquad \| \\ N\!-\!CCH_3 \end{array}$$
This chloride was prepared by heating
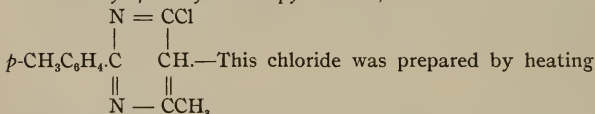
on the steam bath 15 grams of 2-paratolyl-4-methyl-6-oxy-pyrimidine[1] with 17 grams of phosphorus pentachloride and about 20 cc. of phosphorus oxychloride for 7 hours. A dark colored solution was obtained which was slowly poured upon crushed ice to destroy the phosphorus halides. The chlorpy-rimidine separated at once, and crystallized from alcohol in beautiful prisms melting at 107° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{11}N_2Cl$.	Found. I.	II.
N	12.81	12.75	12.83

2-Paratolyl-4-methyl-6-thiocyanpyrimidine,

p-$CH_3C_6H_4C$
$$\begin{array}{cc} N = C.SCN \\ | \qquad | \\ CH.\!- \\ \| \qquad \| \\ N\!-\!CCH_3 \end{array}$$
An alcoholic solution (30 cc.) of 4
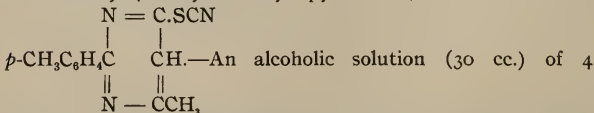
grams of 2-paratolyl-4-methyl-6-chlorpyrimidine and 3 grams

[1] *Loc. cit.*

of potassium thiocyanate was boiled for 1.5 hours. The insoluble potassium chloride was removed by filtration, and the solution cooled, when the thiocyanate separated in irregular prisms. It crystallized from alcohol in fern-shaped crystals melting at 123°. When warmed with aniline or aqueous ammonia at 100° it was recovered unaltered. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{11}N_3S$.	Found.
N	17.42	17.2

2-Paratolyl-4-methyl-6-thiopyrimidine,

$$\begin{array}{c} \text{NH — CS} \\ | \quad\quad | \\ p\text{-}CH_3C_6H_4C \quad\quad CH. \\ || \quad\quad || \\ N \text{——} CCH_3 \end{array}$$
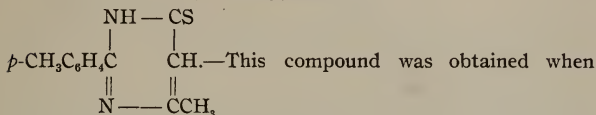
—This compound was obtained when 2-paratolyl-4-methyl-6-thiocyanpyrimidine was gently warmed with one molecular proportion of thiobenzoic acid. It deposited from alcohol in slender prisms melting at 114°. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}N_2S$.	Found.
N	12.96	12.81

Rearrangement of 2-Paratolyl-4-methyl-6-thiocyanpyrimidine into the Isothiocyanate:—One and five-tenths grams of the thiocyanate were heated, in an oil bath, for 2.5 hours at 130°–135°. We obtained a thick oil which slowly crystallized after cooling. The compound was very soluble in warm alcohol and on cooling crystallized in radiating prisms melting at 207°–208°. It did not react with ammonia and a nitrogen determination agreed with the calculated value for the isothiocyanate. It probably is a polymeric form of the isothiocyanate, $(C_{13}H_{11}N_3S)_x$. Analysis (Kjeldahl):

	Calculated for $(C_{13}H_{11}N_3S)_x$.	Found.
N	17.42	17.35

In a second experiment the thiocyanate was heated for 2 hours at 130°–135°, cooled, and then suspended in aqueous ammonia for 2 days. We obtained a yellow amorphous pro-

duct which crystallized from alcohol in irregular prisms melting at 145°–146°. A nitrogen determination agreed with the calculated value for

2-Paratolyl-4-methyl-6-thioureapyrimidine,

$$\begin{array}{c} \text{N} = \text{CNHCSNH}_2 \\ | \quad\quad | \\ p\text{-CH}_3\text{C}_6\text{H}_4\text{C} \quad \text{CH.---} \\ \| \quad\quad \| \\ \text{N} --- \text{CCH}_3 \end{array}$$
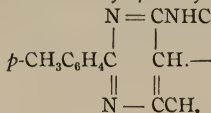
	Calculated for $C_{13}H_{14}N_4S$.	Found.
N	21.70	21.45

2-Paratolyl-4-methyl-6-aminopyrimidine,

$$\begin{array}{c} \text{N} = \text{C.NH}_2 \\ | \quad\quad | \\ p\text{-CH}_3\text{C}_6\text{H}_4\text{C} \quad \text{C.H.} \text{ --- 2-Paratolyl-4-methyl-6-chlorpyrimidine} \\ \| \quad\quad \| \\ \text{N} --- \text{C.CH}_3 \end{array}$$
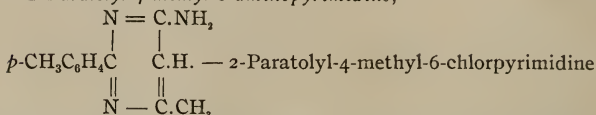
was recovered unaltered after heating with alcoholic ammonia for 2 hours at 120° and again for 2 hours at 150°–160°. When heated with ammonia at 180°–190° for 2 hours a good yield of the aminopyrimidine was obtained. It deposited from alcohol in hexagonal tables melting at 178°–179°. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{13}N_3$.	Found.
N	21.10	21.06

2-Paratolyl-4-methyl-6-anilinopyrimidine,

$$\begin{array}{c} \text{N} = \text{CNHC}_6\text{H}_5 \\ | \quad\quad | \\ p\text{-CH}_3\text{C}_6\text{H}_4\text{C} \quad \text{CH.---The} \quad \text{hydrochloride} \quad \text{of} \quad \text{this} \quad \text{base} \\ \| \quad\quad \| \\ \text{N} --- \text{CCH}_3 \end{array}$$
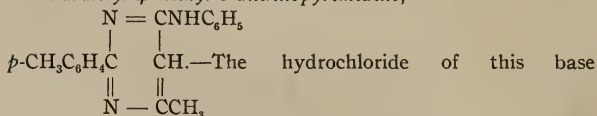
was obtained when 1 gram of 2-paratolyl-4-methyl-6-chlorpyrimidine and 1 gram of aniline were warmed in benzene for 6 hours. The salt crystallized from alcohol in clusters of needles melting at 269°–270° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_{18}H_{17}N_3.HCl$.	Found.
N	13.48	13.44

The base crystallized from alcohol in needles melting at 120°–121° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{18}H_{17}N_3$.	Found.
N	15.27	15.17

NEW HAVEN, CONN.,
March 1, 1908.

STUDIES ON THE SOILS OF THE NORTHERN POR-TION OF THE GREAT PLAINS REGION: NI-TROGEN AND HUMUS.

By FREDERICK J. ALWAY AND ROBERT S. TRUMBULL.

In previous articles[1] of this series it has been shown that in many respects the soils of the northern portion of the great plains region resemble those of the arid portions of California. Among the most characteristic features of the latter are the small amount of humus in the surface soil and the very high nitrogen content[2] of the humus. The percentage of nitrogen in the humus of the arid soils of California varies from 9 to 22 per cent, while that of soils from humid regions rarely exceeds six per cent. In the former, the organic matter of virgin soils is present chiefly in the form of humus.

In this article, the term "humus" is used to designate, not the total organic matter of the soil, but only that portion of it which is soluble in dilute alkalies, the "matière noire" of Grandeau.

The analyses reported below were made by the writers while at the Nebraska Wesleyan University, in order to determine whether the generalizations deduced by Hilgard for the soils of California were applicable to the semiarid prairies of Saskatchewan and Alberta. The samples analyzed were not taken with a view to determining their humus content, which accounts for some of them being taken to a depth of less than one foot.

The samples were taken from such widely separated localities, as shown in the fourth column of the table, that they

[1] THIS JOURNAL, **36**, 580; **37**, 1, 275.
[2] Hilgard: Soils, p. 135.

may safely be considered to be typical of the heavier soils of the whole prairie region of the two provinces. The latitude is not given because it differs by less than two degrees between any two of the localities mentioned.

All the samples were of comparatively heavy soil, varying from loam to very heavy clay, except No. 2, which was of fine sand. No. 10 was taken from the surface of a well beaten trail across the prairie. The garden from which No. 12 was taken had received two heavy applications of stable manure although it had been under cultivation only three years.

The percentage of total nitrogen is fairly high in all except No. 2. The percentage of humus is rather low, although much higher than in the arid soils of California. The nitrogen content of the humus does not differ markedly from that of soils from humid regions. The proportion of the total nitrogen of the soil occurring in the form of humus nitrogen is decidedly low, and probably indicates that humification proceeds comparatively slowly in the two provinces.

From the table, it would seem that the surface soil of the semiarid portions of western Canada possesses the characteristics of humid regions while the subsoil[1] shows the marked peculiarities of the subsoils of other arid regions.

[1] THIS JOURNAL: *Loc. cit.*

No.	Locality	Province	Longitude	Crop at time of sampling.	Depth of sample.	Total N in soil. Per cent.	Humus in soil. Per cent.	Humus N in soil. Per cent.	N in humus. Per cent.	Total N in form of humus N. Per cent.
1	Alameda	Saskatchewan	102°17′	Virgin prairie	0—12 in.	0.18	1.42	0.07	4.93	38.8
2	Carlyle	"	102°17′	"	"	0.10	0.91	0.06	6.59	60.0
3	Indian Head	"	103°40′	"	"	0.28	1.90	0.11	5.79	39.3
4	"	"	"	Western rye grass	"	0.25	2.31	0.13	5.63	52.0
5	"	"	"	Oats	"	0.24	2.45	0.10	4.08	41.6
6	"	"	"	Wheat	"	0.26	1.79	0.09	5.05	34.6
7	"	"	"	"	"	0.22	1.98	0.10	5.05	45.5
8	"	"	"	Summer-fallow	"	0.20	1.02	0.06	5.88	30.0
9	"	"	"	Wheat	"	0.19	1.02	0.06	5.88	31.6
10	Milestone	"	104°29′	Roadway	0—4 in.	0.29	1.85	0.13	7.03	44.8
11	"	"	"	Virgin prairie	0—10 in.	0.19	1.10	0.07	6.36	36.8
12	Belle Plaine	"	105°8′	Garden	0—6 in.	0.30	1.54	0.11	7.14	36.6
13	"	"	"	Virgin prairie	0—6 in.	0.18	0.80	0.05	6.25	27.7
14	"	"	"	"	0—12 in.	0.22	1.09	0.06	5.50	27.3
15	Moose Jaw	"	105°35′	Summer-fallow	"	0.20	1.29	0.07	5.43	35.0
16	"	"	"	"	"	0.20	1.08	0.06	5.55	30.0
17	"	"	"	Wheat	"	0.20	1.20	0.06	5.00	30.0
18	Lethbridge	Alberta	112°47′	Virgin prairie	"	0.22	1.35	0.08	5.93	36.4
19	"	"	112°51′	"	"	0.20	1.55	0.08	5.16	40.0
20	Gleichen	"	112°54′	.	"	0.22	1.90	0.10	5.26	45.4

STEREOISOMERIC CHLORIMIDO ACID ESTERS.

By Willis Stose Hilpert.

In 1890 Hantzsch and Werner[1] announced their theory that the stereoisomerism of the benzilmonoximes and dioximes, proved by V. Meyer[2] and his collaborators, and of the aldoximes, proved by Goldschmidt,[3] is caused by the stereochemical properties of the nitrogen present in these substances. Their ideas extended the theory of van't Hoff and Wislicenus, regarding carbon, to nitrogen. They rest upon the assumption that in certain nitrogen derivatives the three valences of the nitrogen atom are directed towards three corners of an irregular tetrahedron, the fourth corner of which is occupied by the nitrogen atom itself. This assumption led directly to the conclusion that the "cis-trans" stereoisomerism of ethylene derivatives (XHC = CHX) might also occur in certain cases when a double bond exists between nitrogen atoms or between a carbon and a nitrogen atom, as in the case of oximes of the type

$$
\begin{array}{ccc}
R - C - R' & & R - C - R' \\
\| & \text{and} & \| \\
N - X & & X - N.
\end{array}
$$
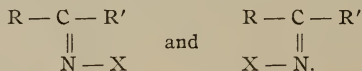
Hantzsch and Werner's theory has proved remarkably fruitful and reliable in explaining the occurrence of stereoisomerism among such derivatives as the oximes, the hydrazones, and diazo bodies, and must be considered as firmly established. If there has been any criticism at all attaching to the theory, it has lain in the unusually large proportion of negative results incidental to efforts to vary the radical X in the above type from the form which it has in the oximes (X = OH; OR'; O — acyl) and hydrazones (X = NHC_6H_5; NRC_6H_5; N — acyl — C_6H_5).

We possibly have some stereoisomeric phenylimide derivatives, but the occurrence of such stereoisomers as claimed

[1] Ber. d. chem. Ges., **23**, 11, 1243 (1890).

[2] Ibid., **16**, 503, 1616, 2176 (1883).

[3] Ibid., **22**, 3113 (1889).

by Schall[1] for modifications of carbodiphenylimides has been challenged; and similarly v. Miller and Plöchl's[2] assumptions of stereoisomerism for certain condensation products of the aldehydeamines have been questioned as not excluding rigorously enough the possibility of structural isomerism. Hantzsch's[3] efforts to obtain stereoisomers in which X was C_6H_5 and other radicals proved fruitless. These negative results have justly been considered as showing the extreme tendency of such compounds to persist in one, the more stable, of a pair of possible stereoisomeric forms. It has, however, always been considered of theoretical importance to obtain stereoisomeric compounds in which X should be as simple as possible and thus limit the cause of the stereoisomerism, experimentally, rigorously to the doubly bound nitrogen and carbon atoms, as it is in the theory. This missing link, fully confirming Hantzsch and Werner's views, was discovered in 1903 by Stieglitz and Earle[4] in the course of investigations concerning the "Beckmann Rearrangement," in which they obtained stereoisomeric methyl chlorimido-*m*-nitrobenzoates, $m\text{-}NO_2C_6H_4C(:NCl)OCH_3$.

In a later investigation carried out with Dr. W. Hale, Stieglitz[5] prepared a second pair of stereoisomers of the corresponding ethyl ester, although only exceedingly small quantities of the one form were obtained; and, in particular, it was discovered that in either of the above cases the less stable stereoisomer can be readily converted into the more stable one by chemical means, namely, by the action of chlorine, the very reagent which one would anticipate as capable of effecting such a transformation.[6]

Only two pairs of such stereoisomers being known, the one form in this case being obtained only in very small quantities, Professor Stieglitz suggested to me to try to discover further representatives of this kind and, in particular, to put

[1] Schall: Z. physik. Chem., **12**, 145 (1893); Ber. d. chem. Ges., **25**, 2883 (1892); J. prakt. Chem., **53**, 149 (1896).

[2] V. Miller and Plöchl: Ber. d. chem. Ges., **25**, 2031 (1892).

[3] *Ibid.*, **28**, 977 (1895); **30**, 3003 (1897); **34**, 822 (1901).

[4] This Journal, **30**, 399 (1903).

[5] The results will be published soon.

[6] See Stieglitz: This Journal. **40**, 42 (1908).

each pair to a rigorous test regarding the proof of the identity of structure and the exclusion of the occurrence of mere physical or crystal isomerism. The results of this investigation, as carried out under his direction, are found in this paper. It may be stated at once that I have obtained five further pairs of stereoisomeric chlorimidoesters, for each of which structural and crystal isomerisms were rigorously excluded, and, that, in fact, stereoisomers were obtained in all but two cases, where a solid chlorimidoester resulted from the action of hypochlorous acid on an imidoester. The five new pairs of stereoisomers are:

Methyl chlorimido-*p*-nitrobenzoate,
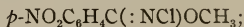
$$p\text{-NO}_2\text{C}_6\text{H}_4\text{C}(:\text{NCl})\text{OCH}_3;$$

Ethyl chlorimido-*p*-nitrobenzoate,

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{C}(:\text{NCl})\text{OC}_2\text{H}_5;$$

Methyl chlorimido-*p*-methyl-*m*-nitrobenzoate,

$$m\text{-NO}_2\text{-}p\text{-CH}_3\text{C}_6\text{H}_3\text{C}(:\text{NCl})\text{OCH}_3;$$
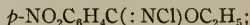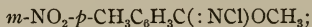
Methyl chlorimido-β-naphthoate, $\text{C}_{10}\text{H}_7\text{C}(:\text{NCl})\text{OCH}_3;$

Ethyl chlorimido-β-naphthoate, $\text{C}_{10}\text{H}_7\text{C}(:\text{NCl})\text{OC}_2\text{H}_5.$

No stereoisomers were obtained in the case of methyl chlorimido-*p*-brom-*m*-nitrobenzoate, and methyl chlorimido-*p*-brombenzoate. The identity of structure was proved in each of the above cases by the action of dry hydrogen chloride, which regenerated from each of the two members of the pair the imidoester hydrochloride that was used in preparing the chlorimides. The imidoester salt was identified by the action of water, leading to an acid ester of a characteristic melting point. The two samples of acid esters obtained from the pair of stereoisomers not only give the same melting point alone, but also give the same melting point when mixed with each other. The actions are as follows:

$$\text{RC}(:\text{NCl})\text{OR}' + \text{HCl} \rightleftarrows \text{RC}(\text{NH}_2\text{Cl})\text{OR}' + \text{Cl}_2;$$

$$\text{RC}(\text{NH}_2\text{Cl})\text{OR}' + \text{H}_2\text{O} \rightleftarrows \text{RCOOR}' + \text{NH}_4\text{Cl}.$$
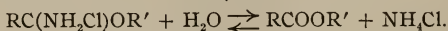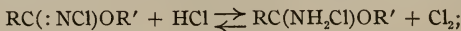
The result proved beyond any doubt that R has the same structure in each of a pair of stereoisomers (for instance, in

regard to the position of a nitro group) and that the group C(: NCl)OR′ also is identical in structure in the pair of isomers. The hydrochloride of the imidoester, when heated, gives an alkyl halide and an acid amide, according to the formulation

$$RC(NH_2Cl)OR' \longrightarrow RCONH_2 + R'Cl.$$

When the acid amide was thus prepared from each of a pair of stereoisomers, it proved to be the same in both cases.

The possibility of having polymeric forms was excluded by the results of molecular weight determinations carried out with two pairs of the above list of stereoisomeric bodies, the simple molecular weight being found in each instance, as was the case in the work of Stieglitz and Earle.

Physical or crystal isomerism was excluded by the fact that each of every pair of stereoisomers maintained its own identity in all changes of physical condition—each crystallizing unchanged from solvents, irrespective of differences of solubility; each crystallizing unchanged after being melted, solidifying unchanged even in contact with a crystal of the other form. In every instance each depresses the other's melting point, usually very considerably; the two forms thus showed complete physical independence of each other. In addition to these methods, which have been employed by Stieglitz and Earle, I was able to prove also that the two stereoisomeric methyl chlorimido-*p*-nitrobenzoates maintain their identity also as gases, each crystallizing, after evaporating *in vacuo*, wholly in its own characteristic form, of characteristic melting point. In fact, under no circumstances was a single transformation observed of one form into the other by physical methods.

So much the more impressive is the fact that, in the case of the first three pairs of stereoisomers mentioned above, it was found possible to transform the less stable stereoisomer into the more stable one by the action of chlorine on the fused chlorimide, the action lasting only two minutes. The explanation given for this transformation[1] suggested at once that it might be reversible to some extent. I was able to

[1] Stieglitz: *Loc. cit.*

bring the complete experimental proof of this anticipated fact in two cases tried, *viz.*, for the two methyl chlorimido-*m*- and *p*-nitrobenzoates, respectively. Chlorine, acting on the naphthalene derivatives, gave gummy products, probably formed by the action of chlorine on the naphthalene nucleus. I found, however, that boiling water transforms one stereo-isomer into the other in this series, and that here too the action is a *reversible one*. The water acts probably by means of traces of chlorine or hypochlorous acid formed from the chlorimide used.

There is no question, then, that the five pairs of chlorimides listed above are true stereoisomers of the "syn" and "anti" type of compounds of Hantzsch and Werner, *viz.*,

$$
\begin{array}{ccc}
\text{R—C—OR'} & & \text{R—C—OR'} \\
\| & \text{and} & \| \\
\text{ClN} & & \text{NCl} \\
\text{(Syn).} & & \text{(Anti).}
\end{array}
$$
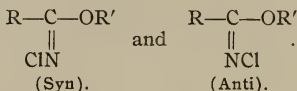
Scarcely any clews have been obtained as to which of each pair should be given the "anti" and which the "syn" configuration. Stieglitz and Hale[1] found in the case of methyl chlorimido-*m*-nitrobenzoate that both pairs suffer to a certain extent a "Beckmann Rearrangement" by destructive distillation above 200°, and their quantitative experiments showed that there is no essential difference in this respect between the two forms. At lower temperatures the compounds are very stable, excepting towards reagents reducing the chlorimido group and thus destroying the cause of stereo-isomerism. The only clew of any value regarding the configuration lies in the following observations: Both for methyl chlorimido-*m*-nitrobenzoate, as found by Stieglitz and Earle, and for methyl chlormido-*p*-nitrobenzoate, as I have found, the *more stable*, so-called β form crystallizes in characteristic plates, has a lower melting point, and is more soluble than the α form, which crystallizes in needles. The β form is readily formed from the α body by the action of chlorine and is always the chief product of the reaction between hy-

[1] Unpublished reports.

pochlorous acid and the free imidoester. Now in both series, for the meta- as for the paranitro acid, the conditions as to stability and yield are absolutely reversed when chlorimido *ethyl* esters are prepared. The stereoisomers crystallize again in characteristic plate and needle forms, but the higher melting needle form (α) is the more stable, and is almost exclusively formed; and the lower melting plate form (β) goes readily over to the needle form (α) by the action of chlorine. This marked change of stability in going from the methyl to the ethyl ester is best explained by the assumption that the β forms have the "anti" configuration,[1] as given above, and that the substitution of the larger ethyl radical for methyl—which should not reverse any condition for chemical or other than physical reasons—crowds out the chlorine atom and makes the "syn" derivatives, by reason of stereochemical considerations, the more stable. It may be added that Werner[2] found that of two stereoisomers of methyl oximidobenzoate, which correspond to our chlorimides, the "anti" form is the more stable one; the "syn" form, crystallizing in needles, goes over readily into the "anti" form:

$$C_6H_5—C—OCH_3 \qquad\qquad C_6H_5—C—OCH_3$$
$$\|\qquad\qquad\qquad\qquad\qquad\qquad \|$$
$$N—OH \qquad\qquad\qquad\qquad HO—N$$

Anti (stable).   Syn (unstable), needles.
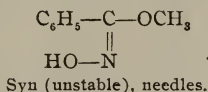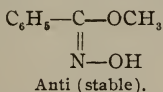
This agrees with the above decisions in regard to the chlorimido methyl esters, *viz.*,

$$m\text{- or } p\text{-}NO_2C_6H_4C—OCH_3 \qquad m\text{- or } p\text{-}NO_2C_6H_4C—OCH_3$$
$$\| \qquad\qquad\qquad \text{and} \qquad\qquad\qquad \|$$
$$N—Cl \qquad\qquad\qquad\qquad\qquad Cl—N$$

β or anti (stable), plates. α or syn (unstable), needles.
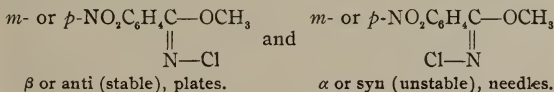
Both the ethyl oximidobenzoates appear to be stable, and neither form, it seems, has as yet been converted into the other.

In the case of the stereoisomeric chlorimidonaphthoates the evidence for determining the configurations is less pronounced, the crystal forms being much alike and no such very decided

[1] "Anti" in regard to the acid radical R.
[2] Ber. d. chem. Ges., **29,** 1158 (1896).

differences in stability of the stereoisomers being apparent.
But still we have the same contrasts as in the pairs discussed.
Of the *methyl* chlorimidonaphthoates, the lower melting, more
soluble form (β) is the chief product of the action,
although a fair yield of the higher melting α form is also ob-
tained. In the case of the ethyl esters, the condition is again
reversed; the higher melting, less soluble α form is again
obtained in larger quantity. So it is very probable that in
these two cases, as in the previous ones, the higher melting
α bodies have the "syn" configuration, and the lower melt-
ing β forms have the "anti" configuration, the "anti" con-
figuration being less favored by the lengthening of the alkyl
from methyl to ethyl.

These configurations are given simply in a *preliminary* way;
further facts will be needed to establish them conclusively.

Repeated attempts were also made by me to prepare stereo-
isomeric pairs of *bromimidoesters*, methyl imido-*m*-nitro-
benzoate and β-naphthoate being used for the purpose; but
all the attempts were futile. It is impossible to say whether
these negative results are due to the greater mass of the bro-
mine atom and consequent greater stereochemical interfer-
ence with the existence of the one stereoisomer,[1] or rather
to the fact that bromimidoesters are much less stable sub-
stances and that any free bromine liberated by the action
of traces of hydrobromic or any other acid would, like chlor-
ine, rapidly change the less stable to the more stable stereo-
isomer. We are inclined to consider the latter the chief
reason for the formation of only one stereoisomer.

In the following pages the most important experimental
results will be given. As the isolation of such sensitive
stereoisomers is dependent on the careful observations of
nice precautions, and the rigorous proof of stereoisomerism
lies in the conscientious, exact exclusion of the possibilities
of structural and physical isomerism and polymerism, it has
been thought best to give the experimental data, when neces-
sary, very explicitly and in detail. This has seemed the more

[1] Victor Meyer showed in his work on stereochemical interference with esteri-
fication and saponification that bromine atoms interfere more than chlorine atoms do.

imperative as in a number of cases apparent crystal iso-
merisms were also observed, *simulating the stereoisomers*,
but fundamentally different from them when critically in-
vestigated.

EXPERIMENTAL PART.

α *and* β *Methyl Chlorimido-m-nitrobenzoate,*

$NO_2.C_6H_4C—OCH_3$ $NO_2C_6H_4C—OCH_3$.—These two esters
$\alpha,$ $\|$, and $\beta,$ $\|$
    $Cl—N$ $N — Cl$

formed the first pair of stereoisomeric chlorimidoesters prepared
by Stieglitz and Earle.[1] The study of these bodies was con-
tinued by me principally in order to determine, more precisely
than had been done, the best quantitative conditions for
obtaining a maximum yield of the less stable stereoisomer, the
α body; and also in order to work out exactly the best method
for a roughly quantitative separation of the two isomers.

In the first experiments, solutions of sodium hypochlorite[2]
were used to convert the imidoester salt into the chlorimide,
from one to nine molecules of hypochlorite being used. The
products obtained were often impure, occasionally oily, refusing
to crystallize, and some were colored. It was suspected that
the excess of free alkali in the hypochlorite mixture prepared
in this way reversed the reaction with the chlorimide, and, by
suppressing the free hypochlorous acid, also interfered with
the formation of the chlorimide. For these reasons it was
thought advisable to use *free* hypochlorous acid, prepared from
sodium carbonate and chlorine according to Erlenmeyer,[3] in
order to secure, in a solution as little acid as possible, the
maximum amount of free hypochlorous acid. One molecule
of chlorine was allowed to react on one molecule of sodium
carbonate at o°. When this mixture was ready, the hydro-
chloride of the imidoester was rapidly dissolved in a little cold
water, immediately treated with a solution of two molecules
of potassium bicarbonate, and this mixture added at once to
the hypochlorous acid solution. The excess of potassium

[1] THIS JOURNAL, **30**, 401 (1903).
[2] Prepared according to Graebe: Ber. d. chem. Ges., **35**, 2750 (1902).
[3] Ann. Chem. (Liebig), **219**, 185.

bicarbonate was used to weaken the acidity of carbonic acid by the presence of an excess of its salt ions.

The first attempt made in this way, three molecules of hyprochlorous acid being used, gave a beautiful, granular product, free from any suggestion of oil or other impurities. By the method of fractionation given below 11.4 per cent (referred to the total crude yield) of α body, melting at 86°, was obtained.

When borax was added with the potassium bicarbonate, with the object of keeping the solution still more nearly neutral, an 8 per cent yield of the α form was obtained.

A 25 per cent yield of the α body was obtained by using a smaller excess of hypochlorous acid, namely, two molecules.

Finally, hypochlorous acid was also prepared by passing chlorine into a suspension of mercuric oxide in water. In one experiment, in which three molecules of acid prepared in this way were used, a yield of 16 per cent of the α body was obtained.

From the results of the above experiments it was obvious that the use of two molecules of hypochlorous acid gave the best yield of the α body, and accordingly this method was adopted in preparing larger quantities of the α modification. The proportions used are as follows: For each gram of the imidoester salt, 3 grams crystallized sodium carbonate and 0.33 gram chlorine were used for the preparation of the hypochlorous acid, and one gram potassium bicarbonate to liberate the imidoester.

In connection with the preparation of larger quantities of the α body, experiments were also made on a roughly quantitative method for separating the α and β forms. Stieglitz and Earle[1] found the α body to be quite soluble in chloroform and hardly soluble in cold ligroin, and so used this as a method for separation, but they do not give any definite proportions of chloroform and ligroin used with a weighed amount of the chlorimide.

The α modification (0.1 gram) was dissolved in 0.5 cc. of chloroform, and 2 cc. ligroin were added, giving a precipitate of needles. Further addition of ligroin gave no more precipi-

[1] *Loc. cit.*

tate. The precipitate weighed 0.08 gram and melted at
86°–87°. This showed that the α body is almost entirely
thrown out of such a chloroform solution by ligroin. One tenth
gram of pure β body was dissolved in 0.5 cc. chloroform and
gave no precipitate at all on the addition of 2 cc. of ligroin.

One tenth gram of the α body with 0.2 gram β form, dissolved
in 1.5 cc. chloroform, were precipitated with 9 cc. of ligroin.
The precipitate weighed 0.05 gram and melted at 86°–87°.

From a solution of 0.1 gram α with 0.2 gram β body in
0.5 cc. chloroform, 2 cc. of ligroin gave a precipitate, 3 cc.
giving a trace more—altogether 0.15 gram—melting at 66°,
and at 61° when mixed with an equal part of the pure α body.
The melting points show that the precipitate had a considerable
quantity of β form present, and that the proportion of chloro-
form must not be reduced.

The best method, then, for separating the chlorimides from
a crude yield is to use 0.5 cc. of chloroform for each 0.1 gram
of the crude chlorimides, and to add four to five volumes of
ligroin. These proportions give the best results as to yield
and purity of the α form, and they were used in the experiment
giving the largest yield of α body, *viz.*, 25 per cent of the crude
yield.

For the preparation of the β form on a large scale, it is best
to convert most of the α body in the crude mixture into the
β compound by the action of chlorine (see below), and then
to fractionate the product by precipitating from a chloroform
solution as much of the α body as possible and allowing the
mother liquor to evaporate. This leaves the β body in a very
pure form. A final method of purification of the β form that
proved successful consisted in dissolving the almost pure body
in very little slightly warm chloroform (less than 0.5 cc. per 0.1
gram chlorimide) and adding seven volumes of ligroin. Only
part of the β body is precipitated by this method, but it is
perfectly pure.

*The Transformation of the Labile α Compound into the Stable
β Body—A Reversible Reaction.*—As proved by Stieglitz and
Earle, the two stereoisomeric chlorimides are not changed from
one form to the other by any physical means. Stieglitz and

Hale,[1] however, succeeded in transforming the α compound into the β body by chemical means, *viz.*, by the action of chlorine. At 90° the transformation is accomplished in one or two minutes; at ordinary temperatures and in chloroform solution only very slowly.

The explanation of this transformation[2] suggested at once that the change ought to be, to a certain extent, a reversible one. To test this view, I allowed chlorine to act separately on absolutely pure α and pure β methyl chlorimidometanitrobenzoates at 90°. Both bodies, especially the β form, were first carefully tested by the same method of fractionation that was to be used after the action of chlorine, and found to be absolutely pure and free from the other isomer.

Pure chlorine, made from potassium permanganate and concentrated hydrochloric acid, was carefully washed with moist beads to free it from traces of acid and then carefully dried by passing it through two tubes of beads wet with concentrated sulphuric acid. The gas, thus treated, was allowed to fill a flask containing 0.2 gram of the pure α body, which was then heated to 90° for two minutes. The α body melted at this temperature and remained liquid during the process. After the action had proceeded for two minutes the substance was cooled and freed from chlorine vapors. The resulting substance melted at 73°–84°, leaving a residue which did not melt.

The whole was then dissolved in as little chloroform as possible and an excess of ligroin added; this gave a slight precipitate of a high melting body, probably a trace of regenerated hydrochloride. The mother liquor of the imidoester, on evaporating, gave crystals on the sides and bottom of the beaker, melting at 81°–82° and 83°–84°, respectively. With equal parts of the α body they melted at 61°–63°, the depression of the melting point showing that no α body was present. With equal parts of the β body the crystals melted at 82°. This showed conclusively that the crystals were the β form. The form of the crystals, as plates, confirmed this conclusion.

[1] Unpublished results.
[2] Stieglitz: This Journal, **40**, 42 (1908).

So, with the exception of the small amount of high melting body, almost all the α body was converted into the β compound.

Half a gram of absolutely pure β body was treated with pure, dry chlorine at 90° for two minutes. The flask was cooled, the chlorine withdrawn, the residue dissolved in 3 cc. of chloroform, and 25 cc. ligroin were added, giving a precipitate similar to that found after the treatment of the α form. The mother liquor gave large plates identical with the β plates, along with smaller crystals on the sides of the beaker. These smaller crystals, weighing 0.135 gram, were dissolved in 0.5 cc. of chloroform and 3 to 4 cc. of ligroin were added. A precipitate was thrown down when the beaker was scratched with a glass rod. Alone, it melted at 84°; mixed with some pure β form, the mixture melted also at 84°, showing the new substance to be identical with the β body.

The crystals from the second mother liquor—only a small amount—melted at 65°–67°. There were enough, however, for analysis by potassium iodide, acid, and sodium thiosulphate for the chlorine content.

0.0254 gram substance gave 0.0041 gram chlorine.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.
Cl	16.52	16.42

This analysis shows that the crystals melting at 65°–67° were pure methyl chlorimido-*m*-nitrobenzoate. Since, then, the crystals were pure and yet had the melting point 65°–67° characteristic of a mixture of the α and β bodies, they must have consisted of such a mixture.[1] We are justified in concluding, then, that some α compound was actually formed by the action of chlorine on the β body.

As the previous experiment proved that after the action of chlorine at 90° the α form would be present only in exceedingly small quantities, the reversal of the action was again attempted in the following way: The α body, if formed, was to be removed as completely as we could, with the minimum possible amount of β body, and the main quantity of the β compound treated repeatedly with chlorine, the α form being continually removed.

[1] Stieglitz and Earle: *Loc. cit.*

Absolutely pure β crystals (melting at 83°–84) were treated with pure dry chlorine for two minutes at 90°. The flask was cooled, freed from chlorine, and the contents extracted with 10 cc. cold ligroin, the ligroin and its vapors removed, the residue again treated with chlorine and again extracted, etc. In this way four extracts were made after four treatments with chlorine; each extract was allowed to evaporate to dryness and gave needles, plates, and mixed crystals.

The needles and mixtures, looking more promising, because of their crystalline form, were examined for the presence of the α body. They were dissolved in very little chloroform and precipitated with ligroin, as usual in obtaining the α form. After a short time a precipitate appeared, which was filtered, washed with ligroin, and dried. The melting point, 86°–87°.5, indicating the presence of the pure α body, its identity was confirmed by the melting point of a mixture of the body with added β body—the melting point was depressed to 62°–63°. Thus the formation of the α form from the β form was established.

Likewise, crystals from the mother liquor of the α precipitate melted at 87°–88°, and mixed with pure α body melted at 85°–87°, showing conclusively again that the crystals above were the α compound. Therefore, by these experiments, it is proved that the action of chlorine on the chlorimides is a reversible reaction.

The Constitution of the Stereoisomers.—It was thought best to confirm the constitution of the α body, as my products were obtained from new preparations of *m*-nitrobenzonitrile entirely distinct from those of Stieglitz and Earle. The same method employed in Stieglitz's and Earle's work was used. One tenth gram pure, dry α body was treated with dry hydrogen chloride in ligroin. This resulted in the formation of a white precipitate of the hydrochloride of methyl imido-*m*-nitrobenzoate. It was filtered, washed with ligroin, and then dried. Part of it was heated to 120° and gave methyl chloride and *m*-nitrobenzamide, melting sharply at 142°. The second part of the hydrochloride was treated with water; it was dissolved to a clear liquid, then in a short time a cloudy precipitate of methyl *m*-ni-

trobenzoate was formed by the decomposition of the imidoester salt. The melting point of the precipitate, 77°–78°, proved the identity of the ester.

These experiments showed that in the α body obtained the methyl group is really attached to the oxygen of the acid radical, and that the nitro group is in the meta position in the benzene radical.

Similarly the constitution of the pure β body was again proved rigorously; it also gave metanitrobenzamide, melting at 140°, and the methyl ester of *m*-nitrobenzoic acid (m. p. 78°), as in the experiment with the α body.

From the experiments it is evident that the bodies worked with have exactly the same structure, that of a methyl ester of chlorimido-*m*-nitrobenzoic acid, and that they must be stereoisomeric chlorimido compounds.

Stereoisomeric Methyl Chlorimidoesters of p-Nitrobenzoic Acid,

$$NO_2C_6H_4C—OCH_3 \qquad and \qquad NO_2C_6H_4C—OCH_3.—$$
$$\|\qquad\qquad\qquad\qquad\qquad\qquad\|$$
$$Cl—N \qquad\qquad\qquad\qquad\qquad N—Cl$$
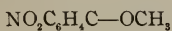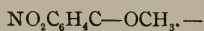
α (syn), needles. \qquad β (anti), plates.

The next body examined for the existence of stereoisomers was methyl chlorimido-*p*-nitrobenzoate.

The nitrile for the preparation of the imidoester salt was obtained from Kahlbaum's *p*-nitrobenzoic acid, m. p. 141°, by successive treatment with phosphorus pentachloride, concentrated ammonium hydroxide, and phosphorus pentoxide. The nitrile was distilled with steam and was found, by its melting point, 147°, to be pure.

The imidoester salt was obtained best from a benzene solution of the nitrile and one and one-tenth molecules of methyl alcohol. The free imidoester was made by liberating it from the aqueous solution of the salt by potassium bicarbonate. It proved to be a white, crystalline body, melting at 93°–94° and readily soluble in hydrochloric acid.

For the preparation of the chlorimide the salt was dissolved in water and twice the calculated amount of potassium bicarbonate solution added. This mixture, containing the free

base, was at once poured into a cold solution of twice the calculated amount of free hypochlorous acid, prepared from chlorine and sodium carbonate. The chlorimide separated immediately, but to give the reaction time to complete itself the mixture was vigorously shaken for several minutes. Then the product was brought on a Hirsch funnel, washed with cold water, and quickly brought on a clay plate.

As a preliminary purification, the chlorimide was dissolved in acetone, in which it is extremely soluble, and reprecipitated by water. The product thus obtained melted at 54°.

A large quantity of the chlorimide was carefully fractionated by the addition of ligroin to the chloroform solution. The chlorimide (2.44 grams) was dissolved in 12 cc. of chloroform, and 40 cc. of ligroin were added. A white, crystalline precipitate resulted, melting at 95°–98°; mixed with some of the plate material (m. p. 76°, see below), it melted below 60°–61°. This characteristic depression of the melting point pointed sharply to the presence of two stereoisomeric bodies.

From the mother liquor of the precipitate, large plates formed, melting at 76°. In the endeavor to get larger yields of the α body, several experiments were made. First 6 times, then 1.25 times the calculated amount of hypochlorous acid was used; thirdly, the hypochlorous acid was warmed to 30°–35°. In no case was the yield of the α body improved. Several more preparations were then made with two molecules of hypochlorous acid in order to get larger amounts of the high melting needles and the low melting plates. The former were repeatedly refractionated by solution in chloroform and precipitation by ligroin, giving, as the highest melting point, 99°–100°. Further fractionation failed to change this melting point, and, as was done in the meta series, the name α body was given to this compound, as the higher melting form.

The other form, crystallizing in plates, gave the constant melting point 76°; it was called the β form. Its crystal form resembles closely that of the β body of the metanitrobenzoate series. It was obtained pure by selecting the clearest looking plates from the crystals left by evaporation of the mother liquors, from which the α form had been precipitated. These

plates were redissolved in a minimal quantity of chloroform and four or five volumes of ligroin added, thus leaving the last traces of the α body in solution and precipitating the β compound, melting at 76°.

A mixture of the two pure crystal varieties invariably melted much lower than either form, usually near 60°.[1]

That these two bodies, with different crystal forms and melting points 24° apart, are stereoisomers rests again on the proof of (a) the identity of their analytical composition; (b) the identity of their structure; (c) the persistence of their separate identity under different physical conditions; and (d) the transformation of one into the other by a rearrangement by means of chlorine.

Upon analysis the following results were obtained:

I. 0.1228 gram substance (α body) gave 0.0200 gram Cl.
II. 0.1486 gram substance (β body) gave 0.0241 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	Found. II.
Cl	16.52	16.34	16.27

These analyses show, then, that as far as empirical composition is concerned, the two bodies have the formula $C_8H_7O_3N_2Cl$.

The identity of structure of the two compounds was proved exactly as in the meta series; namely, by converting each compound back to the imidoester salt, and getting from each the same *p*-nitrobenzamide and *p*-nitrobenzoic methyl ester. Eleven hundredths gram of the pure α body in ligroin was treated with dry hydrogen chloride. The hydrochloride of the imidoester thus formed gave *p*-nitrobenzamide (m. p. 192°–195°) and methyl *p*-nitrobenzoate, which melted at 92°–95°. The melting point of methyl *p*-nitrobenzoate is given as 96°.

To complete the proof of identity, some synthetically prepared methyl *p*-nitrobenzoate was mixed with that prepared above. The mixture melted at 94°–96°, showing that the two bodies are identical.

In exactly the same way, the β body was carried through the process of reversion to the imidoester salt, which gave, under

[1] Approximately equal quantities were mixed for all such tests in this investigation.

treatment by heat, *p*-nitrobenzamide, m. p. 192°–195°; and by water the methyl *p*-nitrobenzoate, m. p. 93°–94°; a mixture with the ester obtained from the α body melted at the same point.

These experiments prove the perfect identity in structure of the α and β forms of methyl chlorimido-*p*-nitrobenzoate, the reactions involved being absolutely the same for both forms and leading to identical products.

The possibility of the needles (α) and the plates (β) being physical isomers or crystal modifications is rigorously excluded by their physical behavior. One form is never converted into the other by the action of physical solvents or by physical contact in solution or in a liquid condition. The α form, melted at 100°, and allowed to cool and solidify, melted again at precisely 100°. The plates melted at 76°, and allowed to solidify, melted again exactly at 76°. A mixture of the two, as has been stated, melts at 60°–61°, and after the mixture has solidified it melts again at 60°–61°, which shows that the two forms preserve their identity even when fused and crystallized together.

A concentrated solution of the pure β body in chloroform gives, on the addition of ligroin, a precipitate of the pure β modification, although the α form is the less soluble of the two and, if present in more than very small quantities, is precipitated first. The two forms preserve their identity, therefore, not only in the solid condition but in the molten and dissolved substances.

Finally the persistence of each form even in the gaseous condition was established as follows: 0.1 gram of the pure α body was heated in a test tube fitted with an inner condensing tube placed about 1 cm. above the substance in order to avoid any decomposition by overheating the compound, since any acid fumes would have evolved chlorine which, in turn, would have caused a rearrangement of the stereoisomers (see below). At 1 mm. pressure boiling commenced at 130°, and soon a sublimate appeared on the sides of the inner tube. After cooling, the sublimate was found to melt at 98°–99°, and mixed with pure α body again melted at 98°–99°, which shows that

even in the gaseous form no change into the β body takes place, the α molecules preserving their identity absolutely. The portion which remained in the bottom of the distilling tube when the distillation was interrupted also consisted of unchanged α body, as proved by the melting point.

Similarly the β body was subjected to a distillation at 1 mm. pressure in a bath at 135°–140°. The substance vaporized and sublimed on the tube as in the case of the α body. The crystals from the bottom of the tube, which had not been distilled, melted at 71°–72°; and those from the cooling tube, which had been formed from the vapor, melted at 73°–74°. Both, when mixed with β body (m. p. 71°–72°), melted at 71°–74°, showing, as in the α body experiment, that vaporizing has no tendency to change one isomer into the other.

As was anticipated, whereas physical methods failed to convert either form into the other, the action of chlorine readily converts the α body into the more stable β stereoisomer, just as traces of hydrogen bromide effect a change of maleic to fumaric acid, and as hydrogen chloride frequently converts one stereoisomeric oxime into the other. It was found, again, that the transformation by chlorine is a reversible one, the more stable β form being obtained in chief quantity but a small amount of the α body being formed even from the purest β form.

Eleven hundredths gram pure α compound was kept in contact with carefully washed and dried chlorine at 94° for four minutes; the product was then cooled and freed from chlorine. It showed a melting point of 69°–70°, indicating a change from the original body. The mass, dissolved in little chloroform and treated with ligroin, gave a very slight precipitate, which was filtered and allowed to dry while the mother liquor evaporated. This precipitate melted high and probably was the hydrochloride of the imidoester. It contained no active chlorine. The crystals obtained from the mother liquor evaporation were plainly the β body, as shown by their crystal plate form; they melted at 75.5°. A mixture of these plates and β body (m. p. 74°) melted at 74°, and after solidifying, it again melted at 74°. So these crystals were beyond

question the β form and proved that by the influence of chlorine the α stereoisomer can be converted into the β form.

As a parallel experiment the action of chlorine on pure β compound was studied to determine whether or not the action of chlorine on the α body is reversible. β crystals (m. p. 76°), whose absolute purity was established not only by their melting point but by the same process of fractionation used on them afterwards to extract the traces of α body formed by the action of chlorine, were heated with pure, dry chlorine at 95° for two minutes. The resulting mass was cooled and freed from chlorine. It was then extracted with a little cold ligroin, and the undissolved residue again subjected to treatment with chlorine and extracted with ligroin. This process was repeated until no more of the mass remained undissolved on treatment with ligroin. By evaporation, the solutions left crystals on the sides and bottoms of the beakers. The crystals on the bottom were obviously, from their form, β crystals, so the greatest attention was centered on the crystals on the sides, among which needle forms could be distinguished.

All the side crystals were collected and fractionated as usual from a chloroform solution by precipitation with ligroin. A precipitate formed which melted at 97°–98°, and, mixed with pure α body, still melted at 98°–99°, but, when mixed with a little pure β body, the melting point was depressed to 70°–71°. These melting points prove absolutely that the above precipitate actually was the α form of the chlorimide.

Therefore we can finally say that the action of chlorine on the α and β forms is a reversible process and that in the rearrangement both isomers are formed, the β form in the larger quantity.

Stereoisomeric Forms of Ethyl Chlorimido-p-nitrobenzoate,

$$NO_2C_6H_4C\text{—}OC_2H_5$$
$$\|$$
$$Cl\text{—}N$$
α (syn), needles.

and

$$NO_2C_6H_4C\text{—}OC_2H_5.\text{—}$$
$$\|$$
$$N\text{—}Cl$$
β (anti), plates.
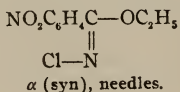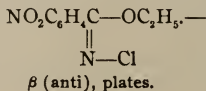
The hydrochloride of ethyl imido-*p*-nitrobenzoate was prepared in the usual way from a chloroform solution of nitrobenzonitrile and 1.1 molecules of ethyl alcohol with the aid of hydrogen chloride.

The chlorimide was prepared, as in the other chlorimide preparations, by the action on the free ester, liberated from the salt by potassium bicarbonate, of hypochlorous acid. For each 3.42 grams of the hydrochloride the hypochlorous acid (2 molecules) formed from 2 grams of chlorine and 9 grams of sodium carbonate in solution as used. The chlorimide separates out easily, as a pure, white, granular precipitate. After being washed and dried, the precipitate was dissolved in chloroform, 3.5 cc. to each 1.0 gram of material, and four volumes of ligroin were added. The precipitate consisted of needles which melted at 95°–96°. The mother liquor gave crystals, principally needles, from the sides, melting at 72°–73°, and from the bottom of the beaker, melting at 88°–93°. Aside from the needles, only two or three very small plate or prism formed crystals appeared on the bottom of the beaker. These plates were carefully taken out and kept separately.

The above crystals (α body) melting at 95°–96° were analyzed and found to be pure ethyl chlorimido-*p*-nitrobenzoate.

0.0668 gram substance gave 0.0102 gram chlorine.

	Calculated for $C_9H_9N_2O_3Cl$.	Found.
Cl	15.50	15.35

It was evident that the needles were the predominant form and that the purest melted at 98°–99°, this being the highest melting point obtained for that form of crystals. They were called the α compound.

While both the precipitated chlorimide and the crystals obtained from the mother liquid were almost exclusively needle shaped, the appearance of the few tiny plates, mentioned above, gave some hopes of isolating a second form. So efforts were made to obtain a larger proportion of the plate form, if possible.

The first attempt was made by treating some of the needles at 95° with chlorine in the hopes of getting a transformation, since in both previous cases chlorine converted the needles almost completely into the more stable plate form. The treatment was continued for five minutes, then the resulting mass was dissolved in chloroform and an excess of ligroin added, throwing down a precipitate of needles, melting at 92°–94°. A few thick plates melting at 81°–85° were obtained from the mother liquid. These latter were also kept separate from the rest of the material. The plates obtained were so few that this method of securing more of the plate form was abandoned.

It was thought that the temperature at which the chlorination of the imidoester salt took place might have an effect on the yield of the plate form. A preparation was made at −5°, and another experiment was carried out at a temperature of 35°. Both preparations gave products similar to those obtained by chlorinating the imidoester at ordinary temperature. After precipitation of the high melting body from the chloroform solutions, the mother liquors, as usual, showed only a very few of the plate forms. Therefore these methods were discarded as a means for getting a larger yield of the plate form of the ethyl ester, and the method of picking out the plates, however few or tiny, whenever they appeared was resumed, and plate after plate collected.

Many times it was observed that crystal mixtures, either as precipitates or mother liquor crystals, which melted low, at 73°–81°, were persistently obtained even after many fractionations. Analyses of these low melting mixtures were made in order to determine whether the depression of the melting point was due to any foreign matter, or to the presence simply of the stereoisomer, which would not alter the analysis. So in each instance of a low melting body an analysis was made. As an example, one precipitate melting at 73°–83° was analyzed with the following result:

0.1185 gram substance gave 0.0183 gram chlorine.

	Calculated for $C_9H_9N_2O_3Cl$.	Found.
Cl	15.50	15.50

This and similar analyses of low melting mixtures proved them to be, in fact, mixtures of stereoisomeric ethyl chlorimido-*p*-nitrobenzoates, which were remarkably difficult to separate.

Low melting mixtures, as above, were dissolved in chloroform and precipitated by ligroin, and, as was expected, several good plates usually formed in the crystal mass left by the mother liquor evaporation. So by continued picking out of individual crystals of the plate form and by careful watching for products which melted low and analyzed well and using them for fractionation, 0.4 to 0.5 gram of the plate form material was finally obtained, as the result of six weeks' collecting.

This material was dissolved in the minimal amount of chloroform, and ligroin was added, giving a precipitate melting at 90°. Equal parts of this material and needles melting at 99°, when mixed, melted at 72°, proving conclusively that the plates or β form, whose highest melting point was observed at 90°, and the α body melting at 99° were two distinct compounds. An analysis of the β form resulted as follows:

0.0530 gram gave 0.0079 gram chlorine.

	Calculated for $C_9H_9O_3N_2Cl$.	Found.
Cl	15.50	14.96

Having shown that the two bodies were isomers and of the formula $C_9H_9O_3N_2Cl$, I next made experiments to prove the identity of their constitutions, exactly as in the case of the other chlorimides studied.

Some of the α form (m. p. 99°), dissolved in chloroform and ligroin, and treated with dry hydrogen chloride, gave a hydrochloride which, with water, formed ethyl *p*-nitrobenzoic ester, m. p. 57°.

The β form (m. p. 90°), treated in the same way, gave exactly the same result.

The chlorimidoesters have therefore exactly the same structure and must be stereoisomers, as in the previous cases.

To find out if the formation of the more unstable body

could be controlled, experiments were made on the effect of chlorine on each of the isomers. The α body (0.43 gram) was treated with chlorine at 100° for two minutes. The resulting product was dissolved in chloroform and precipitated with ligroin. The precipitate, somewhat gummy, melted at 82°–87°, and when mixed with pure β body the melting point dropped to 65°, proving that the precipitate was still the α form. The mother liquor gave crystals melting at 76°–78°, and mixed with the needle forms, m. p. 98°–99°, they melted at 80°–81°. So the mother liquor crystals were not the β form, and by the action of chlorine on the pure α body no decided transformation could be detected.

Some pure β plates, m. p. 90°, were treated with pure dry chlorine at 90°–100°. On cooling, the molten mass solidified quickly, showing that a high melting body was present, rather than a mixture. The mass, under a microscope, looked as if composed of needles only and gave, without further purification, a melting point of 93°. A mixture with pure plates caused the melting point to drop to 73°, again pointing to the presence of chiefly the needle form. Finally, some of the body in question was mixed with the pure α form (m. p. 98°–99°), and the mixture melted at 94°–95°, conclusively showing that the body was the α modification. This shows, then, that the β body is the more unstable, in this case, and is changed by the action of chlorine into the more stable form.

This fact, which is in direct contrast to the relative stability of the needle and plate forms of the methyl ester, and the undoubtedly closely related fact of the decided reversal in the proportions of the two stereoisomers formed by the action of hypochlorous acid on the imidoester, are of importance as giving us the chief means, as yet, of recognizing the actual space structure of the two isomers, as explained in the introduction (p. 155).

n-Propyl Chlorimido-p-nitrobenzoate, $p\text{-}NO_2C_6H_4C(:NCl)OC_3H_7$. —The imidoester hydrochloride was prepared from p-nitrobenzonitrile and 2 molecules of normal propyl alco-

hol in ether solution. The salt is a faintly yellowish, crystalline body, soluble in water.

From this salt the chlorimide was prepared, two molecules of hypochlorous acid being allowed to act on one molecule of the free base, liberated by potassium bicarbonate. The chlorimide proved to be a mobile oil, and all efforts to crystallize it failed.

Stereoisomeric Forms of Methyl Chlorimido-p-methyl-m-nitrobenzoate,

α (syn), plates. β (anti), needles.
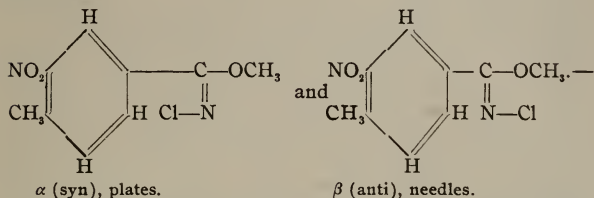
m-Nitro-*p*-methylbenzonitrile was prepared by the action of nitric acid on paratolunitrile, 25 grams of the nitrile being added to a solution of 30 grams potassium nitrate in 500 cc. concentrated sulphuric acid. It was purified by distillation with steam and gave the melting point 99°; Leuckhart, who prepared it by the action of concentrated nitric acid on tolunitrile, gives the melting point as 100°.

The hydrochloride of methyl *m*-nitro-*p*-methylbenzoate was prepared from the nitrile and 1.1 molecules methyl alcohol in chloroform solution. For 10 grams of the nitrile, 40 cc. of chloroform were used to effect solution. The hydrochloride appeared as a white, crystalline body, soluble in water, giving the corresponding methyl ester, and changing to the amide by heat.

The salt was analyzed by a rapid titration with tenth normal sodium hydroxide, phenolphthalein being used as an indicator.[1] 0.4058 gram of the salt required 17.53 cc. of 0.1 N sodium hydroxide.

[1] Miss Barnard, of this labtoraory, has found that these imidoesters are such weak bases that they do not affect phenolphthalein and that their salts can therefore be titrated directly as containing the free acid. The titrations must be carried out rapidly and best from alkalinity to acidity, to avoid decomposition of the salt by water into an acid ester and ammonium chloride which holds the acid in neutral form.

<div align="center">

Calculated for $C_9H_{11}N_2O_3Cl$.   Found.

HCl   15.80   15.75

</div>

The free ester is obtained from an aqueous solution of the hydrochloride by potassium bicarbonate. It is a white, crystalline solid, melting at 60°–61°. It does not affect phenolphthalein, but does affect alizarin sulphonate, not strongly enough, however, for a quantitative determination of it by titration.

Methyl chlorimido-*m*-nitro-*p*-methylbenzoate was prepared from the free ester, liberated from its salt by potassium bicarbonate, with hypochlorous acid, two molecules being used. The crude product, which appeared semisolid and sticky, melted at 43°–44°. It was dissolved in chloroform, and, to separate any less soluble body, ligroin was added. A precipitate formed, which melted at 44°–46°; and crystals from the mother liquor melted also at 44°–46°, while some needles, formed near the bottom of the beaker, melted at 66°–67°. The precipitate, melting at 44°–46°, was analyzed and found to be reasonably pure, showing a chlorine content of 15.23 per cent. The calculated per cent is 15.51. So the precipitate in question was again dissolved in a minimal quantity of chloroform and four volumes of ligroin added. The resulting precipitate now melted at 82°–83°. The crystals from the first mother liquor and from this last one were fractionated again, but no further precipitate resulted. The crystals from the evaporated mother liquors were long, silky needles, mixed with an oily substance. Another fractionation failing to separate the needles from the oil, an analysis for chlorine was made. This gave a low result and showed that the low melting point of the mother liquor crystals in this case was not due to a mutual depression of melting points by two stereoisomers, but to the presence of some foreign substance. This was suspected to be unchanged free imido-ester, as the chlorination had been carried out at a temperature of 5° in order to insure the solidification of the material. The crude material was rechlorinated at room temperature and gave a solid which showed no tendency to liquefy; and

further preparations of the same body, made at room temperature, gave no further difficulty of this kind.

On further fractionation of this purer material, both plate and needle form crystals were observed. Several of the plates were taken out, crystallized, and found to melt at 83°–84°. The needle form crystals melted at 53°–60°. Two crystal forms of the chlorimide having presented themselves, efforts were now directed to getting more of the two distinct forms as pure as possible. Whenever plates appeared they were kept separate and then recrystallized. The needles, likewise, were carefully kept for purification, the crude product containing them chiefly melting at 60°–70°.

The plate material, 1.5 grams, was dissolved in 2.5 cc. chloroform and precipitated with 10 cc. of ligroin. The precipitate melted at 84°–85°, the highest point found for the plate form, which, as the higher melting variety, will be called the α form. To insure its purity, it was again dissolved and precipitated and showed the melting point unaltered, 84°–85°. These plates on analysis gave the following results:

0.0777 gram substance gave 0.0118 gram chlorine.

	Calculated for $C_9H_9O_3N_2Cl$	Found.
Cl	15.51	15.29

This showed, then, that the plate form was pure.

The lower melting needle variety, or β form, 1.3 grams, was dissolved in 1 cc. chloroform and precipitated with 7 cc. ligroin. Then 0.5 cc. chloroform was added to partially dissolve the precipitate in the hope of getting it purer in this way. The precipitate was filtered and found to melt at 71°. The solution was again treated with ligroin and gave a second precipitate, melting at 70°. From another preparation the needles were dissolved in warm ligroin and allowed to crystallize from this solution. The needles last formed melted at 69°–70°. The highest melting point, then, for the pure needle form is 71°.

A mixture of equal parts of the body melting at 83°–84°

with that melting at 71° melted at 53°–54°, giving a depression characteristic of mixtures.

The needle form gave the following analysis:

0.1401 gram substance gave 0.0213 gram chlorine.

	Calculated for $C_9H_9N_2O_3Cl$.	Found.
Cl	15.51	15.23

The analyses having shown that both the needles and the plates had the empirical formula of the chlorimide of methyl 2-nitro-3-methylbenzoate, the identity of their constitution was proved as usual.

Some of the plates in ligroin, treated with dry hydrogen chloride and then with water, formed the methyl ester of 2-nitro-3-methylbenzoic acid, m. p. 47°–48°.

The needles, treated in the same way, gave the same result.

The effect of chlorine on each of the isomers was next studied. A small quantity of plates (m. p. 85°) was treated at 90° for two minutes for pure, dry chlorine. The resulting material melted at 63°–64°. It was dissolved in chloroform and the solution filtered and allowed to evaporate. Needle shaped crystals appeared, melting at 69°–70°. When the needles were mixed with pure plates, the melting point dropped to 54°–55°, showing that the needles were the β form, melting at 70°. It is obvious, then, that under treatment by chlorine the plate (α) form can be changed to the needle formed β body.

Then some of the needle form crystals were heated at 90° for five minutes with chlorine. The resulting substance melted at 64°–65°. It was then extracted with hot ligroin, which, when evaporated, left needles melting at 69°–70°, the melting point of the original crystals acted upon. So by the action of chlorine no appreciable conversion of the needle variety into the plate form is observed; the former is the more stable isomer.

Comparing the properties of this pair of stereoisomeric methyl esters with the stereoisomeric *methyl* chlorimido-esters of *m*- and *p*-nitrobenzoic acids, we note a peculiar contrast in properties; in the latter pairs, the plates repre-

sent the more *stable*, the more *soluble*, and the *lower melting* variety (β form); in the present series the more soluble and lower melting variety (β) is again the more stable one, but it crystallizes in the *needle* form. This contrast in crystal forms complicates the question of the determination of the configuration of the two forms by the method described in the introduction, but as all the properties, other than the crystal form, of the β variety of this pair agree with those of the β forms of the previously described methyl esters, we are inclined, for the present, to ascribe to the present β form, the needles, the same configuration (anti) as to the other β forms of methyl esters described, until further critical material for the determination of configurations can be obtained.

The molecular weights of the two stereoisomers were determined by the cryoscopic method, with benzene as the solvent.

(1) The β body (m. p. 72°), 16.815 grams solvent.

I. 0.2361 gram substance gave 0°.327 depression.[1]

II. 0.5961 gram substance gave 0°.810 depression.

	Calculated for $C_9H_9N_2O_3Cl$.	I.	Found. II.
Molec. Wt.	230.5	227.6	229.0

(2) The α form (m. p. 83°), 15.99 grams solvent.

I. 0.1538 gram substance gave $\begin{Bmatrix} 0°.241^2 \\ 0°.216 \end{Bmatrix}$ depression.

II. 0.3918 gram substance gave 0°.582 depression.

	Calculated for $C_9H_9N_2O_3Cl$.	I.	Found. II.
Molec. Wt.	230.5	236.0 and 211.4	223.1

It is shown, then, by the molecular weight determinations that the chlorimides in question have the formula $C_9H_9O_2N_3Cl$. They are, therefore, neither polymeric nor, as shown above, isomeric forms, the conclusion being confirmed that they are stereoisomers.

[1] The mean of two to four readings is given.

[2] The first reading, 0°.216, is rather far from the mean of other readings, averaging 0°.241; it is reported by itself, as there was reason to consider that the benzene absorbed a trace of moisture after the first reading.

Methyl Chlorimido-p-methylbenzoate,
p-CH_3.C_6H_4C (:NCl)OCH_3, was prepared by chlorinating the corresponding imidoester with two molecules of hypochlorous acid.

The chlorimide appeared as a heavy, colorless oil which showed no signs of crystallizing, even when cooled. On standing two months in a vacuum desiccator it showed no trace of crystals. Under these conditions no attempt to purify the oil was made and it was analyzed in the crude condition.

The following results were obtained for chlorine content:

I. 0.1801 gram substance gave 0.0338 gram chlorine.
II. 0.1383 gram substance gave 0.0258 gram chlorine.

	Calculated for $C_9H_{10}NOCl$.	Found.	
		I.	II.
Cl	19.31	18.79	18.71

Stereoisomeric Forms of Methyl Chlorimido-β-naphthoate,

$$\beta\text{-}C_{10}H_7C\text{—}OCH_3 \quad \text{and} \quad \beta\text{-}C_{10}H_7\text{—}C\text{—}OCH_3.\text{—}$$
$$\underset{Cl\text{—}N}{\|} \qquad\qquad\qquad \underset{N\text{—}Cl}{\|}$$
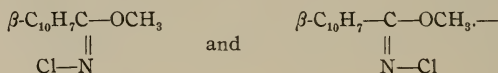
This pair of chlorimides was prepared by chlorinating methyl β-naphthimidoester, obtained from its hydrochloride by potassium bicarbonate. As in previous experiments, the first step to separate possible isomers was made by dissolving the crude product in chloroform and adding ligroin. The precipitate appeared as a white, crystalline body melting at 123°, while from the mother liquor came crystals of a thin, plate form, melting at 66°–67°.

The precipitate, weighing 0.50 gram, was dissolved in 3 cc. of chloroform. From this solution 10 cc. of ligroin precipitated immediately a finely divided, crystalline body melting at 125°, which we will call the α body.

The crystals melting at 66°–67° were extracted with warm ligroin and this solution, on evaporating, left large, thin plates, melting sharply at 72°. This compound will be called the β form.

Recrystallization of each of the bodies melting at 125°

and 72° failed to change their melting points, so these are taken as the melting points of the α and β bodies.

The analyses gave the following results:

I. 0.0786 gram substance (α form) gave 0.0114 gram Cl.
II. 0.1765 gram substance (β form) gave 0.0282 gram Cl.

	Calculated for $C_{12}H_{10}NOCl$.	Found. I.	II.
Cl	16.04	15.79	16.01.

These analyses show, then, that the composition of both bodies is $C_{12}H_{10}NOCl$.

To exclude the possibility of the two bodies being physical or crystal modifications, the melting points of the mixtures were taken. Equal parts of the two bodies melt at 66°; on solidifying and melting again, the mixture showed no change of melting point. A little of the β body with much of the α body melts at 67°; and little of the α form with much of the β body melted at 66°. A little of either, then, can perceptibly lower the melting point of the other.[1]

A quantity of the high melting α body was fused, allowed to cool, and crystallization started by rubbing it with a glass rod covered with a trace of powder of the β body. The solidified substance melted at 125°, showing that the α form maintains its own identity even when crystallizing in the presence of the β form. A similar experiment with the β body proved that it likewise maintains its own identity, m. p. 72°, when crystallizing in the presence of the solid α body. These experiments confirm the conclusion that these isomers can not be mere crystal modifications. The identity of the constitution of the two bodies was also found. Some of the α form, dissolved in ligroin and treated with dry hydrogen chloride, gave an imidoester hydrochloride, from which methyl β-naphthoate, melting at 77°, was obtained. Some synthetically prepared

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[1] The peculiar nature of the depression suggests a closer and quantitative study of the question in this case and that of the ethyl ester, discussed by Dr. Hilpert. It appears possible that the methyl ester (m.p. 72°) is still a solid solution of a *pure* β form and the α form (m.p. 125°). This would account for the particularly large difference in melting points and the small depression of the melting point of the β form. The existence of stereoisomers is not made doubtful thereby, as explained under the ethyl ester.—J. STIEGLITZ.

ester melted at 76° and, when mixed with the above body, still melted at 76°–77°, showing that they are identical.

A parallel experiment to determine the structure of the β body showed that the corresponding product obtained from water melted at 77° and, when mixed with the body obtained similarly in the above experiment, again melted at 77°; mixed with the synthetic body, it melted at 76°–77°. So, beyond any doubt, both the α and β forms have the same constitution.

Molecular weight determinations were also made of the α and β bodies:

(1) The α body (m. p. 125°), 15.19 grams benzene as solvent.

I. 0.1428 gram substance gave 0°.224 depression.

II. 0.3234 gram substance gave 0°.511 depression.

	Calculated for $C_{12}N_{10}NOCl$.	Found I.	II.
Molec. Wt.	219.5	222.5	220.9

(2) The β body (m. p. 72°), 18.87 grams solvent.

I. 0.2242 gram substance gave 0°.290 depression.

II. 0.3234 gram substance gave 0°.450 depression.

	Calculated for $C_{12}H_{10}NOCl$.	Found. I.	II.
Molec. Wt.	219.5	217.0	202.0

In this case the molecular weight determinations bear great weight on account of the great difference in the melting points of the isomers. In no other case studied was there such a great difference in the melting points of two stereoisomers, but the molecular weight determinations set aside all doubt as to the bodies being anything but stereoisomers.

The Reversible Transformation of the Stereoisomers.—The attempt to transform one stereoisomer into the other by the action of chlorine, which had proved uniformly successful with all the pairs of stereoisomers hitherto described, led to the formation of gummy products in the case of the two methyl chlorimidonaphthoates. Such products were obtained by the action of chlorine at 115° on the α body and at 75° on the β form, as well as by the action of chlorine in carbon tetrachloride solution, in the cold, on both bodies. Fractionation with

ligroin did not separate any crystals from the mass, and as both stereoisomers crystallize remarkably well it was evident that other products were formed. The well-known fact that certain naphthalene derivatives form addition products very readily with the halogens points to the absorption of chlorine by the ring carbon atoms as the explanation of the action of chlorine. The nature of the gummy products was not further studied.

The transformation desired was accomplished accidentally and a new method of causing such transformations was discovered as the sequel of a test of the stability of the stereoisomers toward heat, with the object of ascertaining whether in the naphthalene series a "Beckmann rearrangement" would occur more easily than in the benzene series.[1]

The α body was heated to 150°–160° for two minutes. No escape of gas was noticed. After cooling, a sample was taken and found to melt at 115°–117°. The substance was again heated to 188°–190°; this time a slight, sharp odor was perceptible. The resulting material was active toward potassium iodide and acid. To determine whether, by a Beckmann rearrangement, any naphthylisocyanate at all was formed, I heated the product with water for five minutes to convert the isocyanate, if present, into dinaphthylurea. The solutions and solids remaining were extracted with ether, the ether readily dissolving all the solids. The ether, on evaporation, left a crystalline mass melting between 66° and 106°, which was very active in liberating iodine in an acidified iodide solution. This fact and the melting point raised the suspicion that a mixture of the two stereoisomers was present.

By the usual method of fractionation, a fraction was obtained whose melting point indicated unchanged α crystals. A second, more soluble fraction gave crystals melting at 66°, which, mixed with β crystals, melted at 66°–67°. This showed that from the high melting α modification, some of the lower melting β form had actually been formed. No dinaphthyl-carbamide was found.

[1] Stieglitz and Earle: *Loc. cit.*

In a like manner, a quantity of the β modification (m. p. 72°) was heated at 180°–190° for two minutes, a sharp odor being given off. The resulting material was boiled with water and extracted with ether. The residue, left by the evaporation of the ether, melted at 105°–107°. This was fractionated by dissolving in very little chloroform, and the addition of ligroin produced a precipitate which melted at 112°–113°, and, when mixed with the pure α body, at 117°–120°. This melting point proves that some of the β body had been transformed into the higher melting α compound. Crystals from the mother liquor melted at 68°, and, mixed with the β body, at 68°–70°. Therefore a mixture of both the α and β modifications was formed.

To find out just what had caused the transformation, whether the high temperature, the boiling with water, or merely the evaporation in ether solution, a small quantity, 0.10 gram, of the β body was dissolved in ether and the solution allowed to evaporate. The resulting crystals melted at 72°, just as before the treatment; therefore solution in ether causes no transformation, and the bodies are not mere physical isomers. The recovered crystals were boiled a moment with water and heated half an hour on the steam bath. The mixture was then extracted with ether and the crystals resulting from its evaporation were fractionated from 0.5 cc. chloroform and 3–4 cc. of ligroin. The precipitate which formed melted at 96° and, mixed with the α form, at 107°, showing that some change into the α form had taken place. The mother liquor from the precipitate left small, white plates melting at 71°, showing that the remaining substance was the unchanged β body.

Similarly, a control experiment was made on the α body, a small quantity of which was treated with water. The ether extract of the resulting mixture left crystals, which, on fractionating, gave a precipitate melting at 121°. The first crystals from the mother liquor melted at 95°; others, on the sides of the beaker, melted at 65°–67°; and the last, mixed with the β body (m. p. 71°), melted at 66°–70°; proving conclusively that some of the β modification was present.

These experiments showed, first, that the two stereoisomers can be transformed one into the other by a reversible process, a mixture of the two resulting either from the pure α or the pure β body; and second, that the transformation is caused essentially by heating with water. Since dry heat alone has no such effect, it is practically certain that the transformation is produced by the action of a trace of hypochlorous acid or chlorine produced by the action of water on the chlorimidoester, this trace acting, then, as did the chlorine in all the previous transformation experiments, probably through the intermediate formation of an addition product:

$$\begin{array}{ccc}
\underset{\substack{\| \\ N—Cl}}{C_{10}H_7C—OCH_3} + HOCl \rightleftarrows & \underset{\substack{\diagup\diagdown \\ HO\quad N—Cl \\ | \\ Cl}}{C_{10}H_7C—OCH_3} \rightleftarrows & \underset{\substack{\| \\ Cl—N}}{C_{10}H_7—C—OCH_3} + HOCl.
\end{array}$$
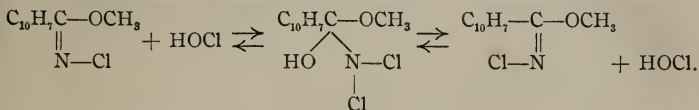
The transformation is considered particularly important on account of the great difference in the melting points of the two stereoisomers.

The Stereoisomeric Forms of Ethyl Chlorimido-β-naphthoate,

$$\underset{\substack{\| \\ N—Cl}}{C_{10}H_7—C—OC_2H_5} \quad \text{and} \quad \underset{\substack{\| \\ Cl—N}}{C_{10}H_7—C—OC_2H_5.} —$$
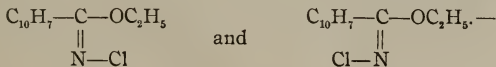
Slosson,[1] working in this laboratory, prepared ethyl chlorimido-β-naphthoate by the action of bleaching powder on ethyl imido-β-naphthoate, and described it as a well crystallizing substance of melting point 71°, *forming needles and plates* by crystallization from warm ligroin. With the object of getting these needles and plates and separating them, mechanically, if need be, I prepared the body from chloride of lime solution, exactly as described by Slosson, as well as several times by the use of hypochlorous acid prepared by the method described in these pages. Crystals melting at 64°–65° were readily obtained as the first fraction by the first crystallization of the crude product, and by further crystallization the substance of melting point 72° was obtained.

[1] Slosson: This Journal, **29**, 289 (1903).

The needles and plates, however, proved to be the same substance, of the same melting point. The plates were exceedingly thin lamellae and looked like needles at certain angles, and under the microscope no essential difference between the two forms could be noted. These, then, were not stereoisomeric forms. Nevertheless, the formation and presence of stereoisomers in the reaction product was established conclusively, as follows: from the action of hypochlorous acid on the free ethyl imido-β-naphthoate, a product results which, without fractionation, almost invariably melts as low as 36°–39°, and which nevertheless gives, on analysis, excellent figures for a pure ethyl chlorimido-β-naphthoate. For instance, in one case the following result was obtained for crystals melting at 39°:

0.1117 gram substance gave 0.0168 gram chlorine.

	Calculated for $C_{13}H_{12}NOCl$.	Found.
Cl	15.17	15.06

For further purification this product (3 grams) was extracted with 35 cc. of warm ligroin. The solution, on evaporating, left crystals melting at 64°–65° on the bottom of the beaker, and the last crystals to appear, on the sides, melted at 38°–48°. The first crystals (m. p. 64°–65°), after several fractionations, gave a product which melted constantly at 72°. This substance, which was described and analyzed by Slosson, will be called the α form, and is most likely the syn stereoisomer (see above[1]). The low melting crystals were all collected and extracted with ligroin and the solution allowed to evaporate. At first, on cooling, needles formed, which melted at 38°; and the crystals forming later on the sides of the beaker melted at 37°–39°. When about one half the liquor had evaporated, it was decanted and allowed to evaporate further in another beaker. After a time, tufts of needles appeared, which melted between 39° and 47°. The solution was again decanted and allowed to evaporate. More of the crystals melting between 39° and 48° appeared. An analysis of the latter crystals was made and yielded the following results:

[1] Page 156.

0.1198 gram substance gave 0.0179 gram Cl.

	Calculated for $C_{13}H_{12}NOCl$.	Found.
Cl	15.17	14.96

The crystals melting at 39°–48°, when mixed with an equal quantity of the body melting at 72°, melted *completely* at 39°–41°, showing a lowering of about 7° for part of the substance, which pointed to a difference in the two bodies.

The mixture of crystals melting at 38°–40° were repeatedly extracted with ligroin, and finally a product melting constantly at 39° was obtained. As will be shown presently, the substance of the low melting point (39°) has exactly the same structure as the compound melting at 72°; and the analyses given above, proving its purity beyond a doubt, show that *no foreign impurity* is the cause of the low melting point. The body melting at 39° must then unquestionably be either the second stereoisomeric (β) form itself or, more likely, a mixture of two stereoisomeric forms, one of which melts at 72°, while the second could not be completely separated from its stereoisomer, owing to the great solubility of the two forms, even in ligroin, saturated solutions of the two forms in each other giving the minimum melting point 39°. We are inclined to hold that the substance is not the pure β form, but rather a mixture, as described, of the α and β forms, and that the pure β compound melts at 48° or higher. The following facts lead us to this belief:

(1) The melting point of the fractions melting between 39° and 48° is depressed by the α form.

(2) The α form does not depress the melting point below 39°, as it would if the substance melting at 39° did not already contain the α body mixed with the β compound.

(3) The existence of a minimum melting point corresponds perfectly to the minimum melting points observed for the mixture of the two stereoisomers in every other series. The only difference between the behavior of this mixture and all the others lies in the impossibility of separating the two stereoisomers completely; but as the more insoluble α form was isolated and found to melt at 72°, there can be no question

that in the substance melting at 39° the second stereoisomer must be present. It may be recalled that the discovery of the stereoisomers of the chlorimide of methyl *m*-nitrobenzoate started from the same initial fact that a mixture, giving perfect analyses, melted 30° lower than the fractionated product, and that the second stereoisomer, whose presence was deduced from this behavior, was found in short order. For these reasons it is considered that the above behavior proves that ethylchlorimido-β-naphthoate also exists in two stereoisomeric forms.

The proof that the α and β forms have the same constitution was brought, as in the cases of the other stereoisomeric chlorimides, by converting the chlorimides into the hydrochloride of the imidoester and decomposing the salt by water into ammonium chloride and the ethyl ester of β-naphthoic acid, and by converting the salt into β-naphthylamide and ethyl chloride by heat.

The ethyl naphthoate obtained from the α body (m. p. 72°) and from the α, β mixture (m. p. 39°) melted at blood temperature, and mixtures of the two did likewise. This indicated that the ethyl group is attached to oxygen in these bodies, also that they both have the same structural formula. A second rigorous proof was obtained by heating the hydrochlorides of the imidoester, obtained by passing dry hydrogen chloride into a ligroin solution of the mixture melting at 39° and also of the α body. Both hydrochlorides decomposed at 135°, leaving residues melting sharply at 191°–192°, the melting point of β-naphthamide. A mixture of equal parts of the β-naphthamide (m. p. 191°–192°) formed from the α body and that formed from the α, β mixture melted also at 191°–192°. This, then, proves unquestionably that in this chlorimide, both in the α body (m. p. 72°) and in the α, β mixture (m. p. 39°), we have compounds of the same structure and composition.

Since, then the two bodies have different melting points and analyze as pure $C_{13}H_{12}NOCl$, and both have the same structure, we must have two stereoisomers.

The ethyl chlorimidonaphthoate is the last chlorimidoester

examined for which I have been able to establish the existence of a pair of stereoisomeric esters. Some experiments with two other chlorimidoesters and two bromimidoesters, which in spite of the scrupulous application of the same methods of preparation, fractionation, and transformation, gave negative results, are of peculiar interest as showing the difficulties attending the formation of such isomers. In view of the formation of the stable variety in considerable excess, in all the above cases, and of the transforming effect of chlorine and, undoubtedly, also of hypochlorous acid, and, finally, in consideration of the sharp and characteristic indications of the occurrence of stereoismerism, as shown in the study of melting points, which makes it comparatively easy now to recognize its occurrence, we are led to conclude that the failure to obtain stereoisomers is probably due less to difficulties in separating any stereoisomers than to the fact that the stable form must be favored to such an extent in the preparation that the unstable one is scarcely present, if at all. A failure to establish the existence of stereoisomers for a solid chlorimidoester is limited to two cases. More important and interesting is the fact that all endeavors to prepare stereoisomeric bromimidoesters have thus far been unsuccessful, the last attempt having been made with methyl β-naphthoate, for which the corresponding chlorimide stereoisomers melt 50° apart.[1] The theoretical significance of these facts having been discussed in the introduction, the experimental results for these compounds will be briefly given.

Methyl Chlorimido-p-brombenzoate, p-$BrC_6H_4C(:NCl)OCH_3$.[2] —This chlorimide was prepared by chlorinating the corresponding imidoester with two molecules of hypochlorus acid. The chlorimide appeared at first as an oil, which solidified only on freezing.

The solid, oily mass was dissolved in warm ligroin, and when the solution cooled, a precipitate settled out. This

[1] See note, p. 179

[2] The imidoester was obtained from p-brombenzonitrile, which was prepared from p-brombenzoic acid (Kahlbaum's preparation) by the successive treatment with phosphorus pentachloride, ammonia, and phosphorus pentoxide.

precipitate melted at 57°.5, and the crystals from the mother liquor, branches of needles, melted at 54°–55°.

More of the crude chlorimide, dissolved in chloroform, failed to give a precipitate on the addition of ligroin. This solution, on evaporating, gave crystals which were rubbed up with cold ligroin to take out the more soluble portion, and filtered. These crystals melted at 58°–59°, and the crystals from the mother liquor, plates, melted at 60°.

The plates melting at 60°, mixed with the body melting at 58°–59°, melted at 58°–59°, and when mixed with the needles melting at 55°, at 56°–57°. The plates and needles, therefore, cannot be considered as representing stereoisomeric substances, but rather two crystal or physical modifications of a single substance, as no depression of the melting point occurs when they are mixed. Such a case is not uncommon with the chlorimidoesters, as will be discussed more fully in connection with the next compound studied, and it shows how the presence of stereoisomers may be simulated by crystal modifications. The analysis of the body showed it to be pure.

0.0518 gram substance gave 0.0073 gram chlorine.

	Calculated for $C_8H_7NOClBr$.	Found.
Cl	14.26	14.26

Methyl Chlorimido-m-nitro-p-brombenzoate,
p-Br-m-$(NO_2)C_6H_3C:(NCl)OCH_3$. Although the investigation of the chlorimide prepared from methyl imido-p-brom-m-nitro-benzoate[1] did not lead to the isolation of a further pair of stereo-isomers, it proved particularly instructive as emphasizing the difference in behavior of two crystal forms of a single substance and of two stereoisomers in the critical tests used. The new chlorimide was observed to occur in two modifica-tions, crystallizing sometimes as needles, sometimes as plates, just like some of the stereoisomers previously described. Low melting fractions were also very frequently obtained. But the following vital differences in behavior, in the present case, were observed: (1) the low melting frac-

[1] The hydrochloride of the imidoester was obtained in the usual way from m-nitro-p-brombenzonitrile. The nitrile was obtained from p-brombenzonitrile by Schöpff's method (Ber. d. chem. Ges., **23**, 3439 (1890)).

tions invariably gave quite low results when analyzed for active chlorine, which showed that the depression of the melting point could have been largely, or altogether, due to some foreign substance (probably some nonchlorinated imidoester); (2) the melting points of these low melting fractions were invariably raised by admixture of the pure chlorimide; (3) no depression of the melting point is observed when the melting point of a mixture of needles and plates is taken; (4) one and the same material, on recrystallization, was obtained sometimes in the form of needles, sometimes as massive plates, according to the method of crystallization. This is the behavior of physical modifications of a substance, and, by contrast to the fundamentally different behavior of the stereoisomers isolated, confirms our conclusions regarding the latter.

The following statement of a part of the experimental results obtained will be sufficient to serve as a foundation for the above parallel. A light yellow solid resulted when methyl imidobromnitrobenzoate was treated with hypochlorous acid. The crude product, 3 grams, was dissolved in 6 cc. chloroform, and on the addition of 21 cc. ligroin a precipitate was thrown down, melting at 89°–90°. From the mother liquor needles melting at 56°–63° and plates melting at 89°–90° were obtained. The precipitate and plates melting at 89°–90° gave the same melting point when mixed. The two were dissolved together in 3.5 cc. chloroform and 20 cc. ligroin were added, producing a precipitate of *needles* melting at 95°, while plates (m. p. 90°) were obtained from the mother liquor. The needles and plates, mixed, melted at 92°–93°. The needles (m. p. 95°) were analyzed with the following result:

0.0946 gram substance gave 0.019 gram chlorine.

	Calculated for $C_8H_6N_2O_3ClBr$.	Found.
Cl	12.07	11.80

Both needles and plates were obtained showing low melting points ranging between 59° and 90°, and in either case the melting point was raised by the admixture of pure substance, m. p. 94°–95°. An analysis of such low melting needles (59°–66°) gave a chlorine content of 11.37 per cent (calculated

12.07). It is obvious from these facts that we would not be justified in considering the plates and needles as representing stereoisomeric forms in this case. This conclusion, nevertheless, does not of course, exclude the possibility of two stereoisomers existing, it will be recalled that one of the first pair of stereoisomers discussed, the α form of methyl chlorimido-*m*-nitrobenzoate, crystallizes in two forms, usually forming silky needles, but yielding rectangular plates by slow evaporation of its solutions, both these forms being entirely different from the third form, the stereoisomeric β body[1]. But, in the present case, we simply have one of the many well-known instances of the formation of a stable stereoisomer in such preponderance that the less stable form is either not produced at all or in such slight amount that it becomes exceedingly difficult to isolate it. As was to be expected, the action of chlorine on our product (m. p. 94°–95°) proved it to be the stable form, most of the body being recovered unchanged. A small fraction was obtained melting between 66°–79°, and as only pure chlorimide was used, it may very well be that a small amount of a less stable stereoisomer was formed, as was rigorously proved in previous cases; but the material was insufficient for any present attempt to isolate the missing stereoisomer.

Methyl Chlorimido-p-anisate, p-CH_3O-C_6H_4C(: NCl)OCH_3.—The hydrochloride of methyl imidoanisate was prepared from anisonitrile, which was readily obtained from the acid, by way of the chloride and the amide.

0.2772 gram of substance gave 0.0500 gram HCl.

	Calculated for $C_9H_{10}NO_2Cl$.	Found.
HCl	18.08	18.07

The anisic imidoester was then liberated by potassium bicarbonate and chlorinated with two molecules of hypochlorous acid. The product was a faintly yellow oil, with a sharp odor. All efforts to crystallize it by cooling or other mechanical means failed. The oil was analyzed as follows:

0.2526 gram substance gave 0.0448 gram Cl.

	Calculated for $C_9H_{10}NO_2Cl$.	Found.
Cl	17.76	17.66

[1] Stieglitz and Earle: *Loc. cit.*, p. 403.

Methyl Bromimido-m-nitrobenzoate, $m\text{-}NO_2C_6H_4C(:NBr)OCH_3$.
—The first attempts to prepare a pair of stereoisomeric brom-
imidoesters were made with methyl imido-*m*-nitrobenzoate,
from which Stieglitz and Earle had obtained the first pair
of chlorimidoesters. Hypobromous acid was used as the re-
agent. It was obtained by the action of bromine on sodium
hydroxide, the latter usually in slight excess beyond that
required by the formulation

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O.$$
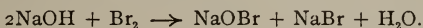
The action with the imidoester hydrochloride is as follows:

$$NaOBr + NO_2C_6H_4C(NH_2Cl)OCH_3 \longrightarrow$$
$$NaCl + H_2O + NO_2C_6H_4C(NBr)OCH_3.$$
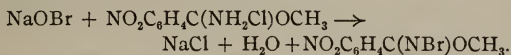
A large excess of alkali reverses this action, giving a very
impure product; less alkali was not used because of the trans-
forming power of the free halogen. But a considerable ex-
cess of hypobromite was occasionally used with the object
of hastening the action by mass action, so as to separate
as quickly as possibly any unstable, solid bromide which
might be formed. Several preparations were made in which
the hypobromite was varied from one to eight molecules.
The former gave yellowish precipitates of low melting points
(*e. g.*, 37°) and even oils, but they were very impure, as shown
by analysis, and little could be done with these products,
which unquestionably contained unchanged free imidoester.
The large excess (8 molecules) of hypobromite gave at once
a good yield of flocculent precipitate, only slightly colored.
It was dried and dissolved in ligroin, and the solution allowed
to evaporate. There appeared, after a time, large plates
melting at 95°. There were also needles, in one case, melt-
ing at 83°, and, in another, at 91°. These two apparently
different forms gave a little hope of finding stereoisomers.
More of the bromimide was then prepared as above, and again
extracted with ligroin and then chloroform. On letting
the ligroin evaporate till crystals appeared and decanting the
supernatant liquor, several fractions were obtained. In the
first fraction, plates melting at 97°–98°, along with needles

melting at 86°–87°, were found. These latter, mixed with equal parts of the plates, still melted at 86°, showing them to be, most likely, different crystal forms of the same body.

Another method of purifying the crude bromimide was to dissolve the substance in acetone and precipitate it with water.

From several ligroin extracts both needles and plates were obtained, and when the needles were again recrystallized from ligroin and chloroform, besides needles, some plates appeared when nearly all the solution was evaporated. The needles are seen under a microscope *to have the same end angles* as the plates. The recrystallized needles melted at 101°. After recrystallizing the needles once more it was found that their melting point remained constant. The analysis of the body melting at 101°, of which very little was obtained, resulted as follows:

0.0074 gram substance gave 0.0049 gram bromine.

	Calculated for $C_8H_7N_2O_3Br$.	Found.
Br	30.88	30.43

The plate form crystals were also recrystallized from ligroin and chloroform. On evaporation of the solution, both needles and plates remained, the needles melting at 97° and the plates at 91°. The plates, after being pulverized and leached with ligroin, melted at 96°. Then they were recrystallized from ligroin once more and gave the melting point 99°.9.

A mixture of the plates (99°.5) and the needles (101°) melted at 99°–100°, showing identity and therefore absence of stereoisomers.

From these experiments it was concluded that the needles and plates obtained are not stereoisomeric forms, as in the case of the chlorimides. They have the *appearance* of crystal varieties, but lack the criteria of stereoisomeric forms: needles are obtained from ligroin solutions and plates are formed when chloroform is present, due, probably, to the slower evaporation; both forms appear under the microscope to have the *same crystalline structure.* The most critical test

of all, the fact that there was no characteristic depression of melting points when a mixture of plates and needles was used, emphasizes the total differences in the behavior of the chlorimides and the bromide.

In order not to overlook the possibility that the bromimide formed might be the unstable modification, although this was scarcely likely, a small amount of the bromimide was heated in a tube to 100° for one half hour in the presence of bromine vapors. In a second similar experiment the bromimide was kept at 100° for *two* minutes; in another, at 95° for two minutes; and in a final one, at 120° for one minute; all gave the original bromimide. Therefore it can be stated that as far as the above experiments go, no stereoisomers of methyl bromimido-*m*-nitrobenzoate were found.

Half a year later, still other experiments were made, the method being employed which was used most successfully in preparing stereoisomeric chlorimides, *viz.*, the use of hypobromous acid made from bromine and sodium carbonate or bromine and a suspension of mercuric oxide in water. The free ester was liberated from its salt by potassium bicarbonate and borax and treated with the hypobromous acid, prepared as above. The bromimide always appeared as a solid and gave good yields of a product of a high degree of purity, but, as in the initial experiments, no stereoisomers could be isolated; in fact, identity was proved, just as before, by the melting points.

The following are analyses of several preparations of the methyl *m*-nitro-bromimidoester:

I.   0.1135 gram substance gave 0.0346 gram Br.
II. 0.0734 gram substance gave 0.0227 gram Br.
III. 0.1550 gram substance gave 0.0475 gram Br.
IV. 0.1947 gram substance gave 0.0603 gram Br.

	Calculated for $C_8H_7O_3N_2Br$.	I.	II.	III.	IV.
Br	30.89	30.49	30.92	30.65	30.96.

Methyl Bromimido-β-naphthoate, $\beta\text{-}C_{10}H_7C(:NBr)OCH_3$.

Because of the very great difference in the melting points and solubility of the stereoisomeric methyl chlorimidonaph-

thoates, it was thought that if stereoisomeric methyl bromimidonaphthoates existed, they would also probably be widely different as to solubility and melting points, and so be easily isolated.

The bromimide was prepared from the hydrochloride of methyl imidonaphthoate by treatment with hypobromous acid, the free ester being liberated by potassium bicarbonate.

The product was a light yellow, granular precipitate, melting at 98°–99°. Three grams were dissolved in 10 cc. of chloroform and then 40 cc. of ligroin were added, giving a crystalline precipitate melting at 99°–100°. The mother liquor gave crystals on the sides and bottoms of three beakers, melting practically at the same temperature, 97°–98°, 96°–97°, and 95°. Each, when mixed with the higher melting body, melted unchanged or higher, showing that all the different products were identical and that no stereoisomers were present.

An attempt was made to transform the bromimide by means of hot water, but the substance was decomposed, one of the products of decomposition being β-naphthamide.

The introductory statement contains a complete summary of the results and conclusions reached, and reference is made to it at this place.

In conclusion, I wish to take this opportunity to express my gratitude to Professor Stieglitz for his careful supervision of this work and for his personal inspiration.

CHICAGO, September, 1907.

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 15°.[1]

BY H. N. MORSE AND B. MEARS.

The measurements of the osmotic pressure of cane sugar solutions at 15°, like those of cane sugar at 10°,[2] and of glu-

cose at the same temperature,[1] are characterized by the min-
uteness of the loss in rotation which the solutions suffered
while in the cells, and likewise by the constancy of the tem-
perature which was maintained in the bath. The bearing of
these factors upon the accuracy of the results has been so
often discussed in these papers that it is necessary now only
to recall the fact—which cannot be too strongly emphasized—
that the principal obstacles to the exact measurement of
osmotic pressure are "*thermometer effects*," and the *dilution
of the cell contents* under conditions which make it impossi-
ble to determine whether, and to what extent, such dilution
preceded or *followed* the measurement. With reasonable skill
and patience, all other known sources of error can be brought
under fairly good control, but the suppression of these has
cost us several years of continuous effort. The beneficial
result of this elimination of the largest and most obstinate
sources of uncertainty will be seen in the latter part of this
paper, where it is shown that the osmotic pressure of cane
sugar solutions has a decided temperature coefficient, a fact
which could not be established while the possible experimen-
tal errors were still large.

The customary duplicate determinations of ten concentra-
tions of solution, ranging from 0.1 to 1.0 weight normal,
have been made, and the results of the individual experi-
ments are given in Tables I. to XX. In the tables which
follow (XXI. and XXII.), these are summarized in the usual
ways:

[1] This Journal, **40**, 1.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.05 mm. Cell used, G. Resistance of membrane, 535,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.43; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.96. Time of setting up cell, 3.00 P.M., Apr. 9, 1908.

Time.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Apr. 11.						
3.30 P.M.	$15°.0$	$15°.0$	143.77	2.47	2.35	0.12
Apr. 12.						
9.00 A.M.	$15°.0$	$14°.8$	143.25	2.46	2.35	0.11
				2.47	2.35	0.12

Molecular osmotic pressure, 24.65.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.049.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.01 mm. Cell used, A₃. Resistance of membrane, 28,421. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.13. Time of setting up cell, 4.00 P.M., Apr. 28, 1908.

Time.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Apr. 29.						
10.00 P.M.	$15°.0$	$15°.6$	158.29	(2.46)	2.35	....
Apr. 30.						
8.30 A.M.	$15°.0$	$15°.8$	157.27	2.48	2.35	0.13
12.30 P.M.	$15°.0$	$15°.4$	157.61	2.48	2.35	0.13
2.30 P.M.	$15°.0$	$15°.6$	157.37	2.49	2.35	0.14
				2.48	2.35	0.13

Molecular osmotic pressure, 24.83.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.056.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 24°.9; (2) at conclusion of expr., 24°.8; loss, 0°.1 = 0.4 per cent. *Manometer:* No. 11; volume of nitrogen, 465.94; displacement, 0.01 mm. Cell used, G. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.48; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.19. Time of setting up cell, 4.00 P.M., May 7, 1907.

Time. May 7.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	14°.8	15°.0	86.11	4.90	4.70	0.20
May 8.						
12.30 P.M.	15°.1	15°.8	85.85	4.92	4.70	0.22
4.00 P.M.	14°.8	15°.3	85.85	4.92	4.70	0.22
May 9.						
12.00 M.	14°.9	15°.2	86.06	4.90	4.70	0.20
				4.91	4.70	0.21

Molecular osmotic pressure, 24.55.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.044.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 25°.0; (2) at conclusion of expr., 25°.0; loss, 0. *Manometer:* No. 24; volume of nitrogen, 472.58; displacement, 0.06 mm. Cell used, B₃. Resistance of membrane, 377,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.26. Time of setting up cell, 12.00 M., May 3, 1908.

Time. May 4.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
8.30 A.M.	15°.0	15°.0	88.66	4.89	4.70	0.19
12.30 P.M.	15°.0	14°.9	88.63	4.89	4.70	0.19
10.00 P.M.	15°.0	15°.0	88.34	4.91	4.70	0.21
May 5.						
8.30 A.M.	15°.0	15°.0	88.64	4.89	4.70	0.19
				4.90	4.70	0.20

Molecular osmotic pressure, 24.50.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.043.

Table V.

0.3 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 36°.6; (2) at conclusion of expr., 36°.6; loss, 0. *Manometer:* No. 21; volume of nitrogen, 477.75; displacement, 0.28 mm. Cell used, B. Resistance of membrane, 367,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.9. Time of setting up cell, 12.30 P.M., May 11, 1907.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 11.						
8.00 P.M.	15°.1	16°.6	61.29	7.32	7.05	0.27
May 12.						
12.00 M.	15°.1	15°.1	61.43	7.30	7.05	0.25
May 13.						
9.00 A.M.	15°.0	15°.2	61.31	7.30	7.05	0.25
				7.31	7.05	0.26

Molecular osmotic pressure, 24.37.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.037.

Table VI.

0.3 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 36°.7; (2) at conclusion of expr., 36°.7; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.04 mm. Cell used, B₃. Resistance of membrane, 224,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.6. Time of setting up cell, 5.00 P.M., May 8, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 9.						
8.30 A.M.	15°.0	15°.0	60.97	7.37	7.05	0.32
May 10.						
1.00 A.M.	15°.0	15°.1	61.18	7.34	7.05	0.29
11.00 P.M.	15°.0	15°.2	61.10	7.34	7.05	0.29
				7.35	7.05	0.30

Molecular osmotic pressure, 24.50.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.043.

Table VII.

o.4 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 47.9; (2) at conclusion of expr., 47°.9; loss, o. *Manometer:* No. 13; volume of nitrogen, 438.84; displacement, 0.02 mm. Cell used, B₃. Resistance of membrane, 560,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 8.17. Time of setting up cell, 4.00 P.M., May 16, 1908.

Time.	Temperature.		Volume	Pressure.		
	Solution.	Manometer.	N₂.	Osmotic.	Gas.	Difference.
May 17.						
12.00 M.	15°.0	15°.8	42.70	9.77	9.40	0.37
4.00 P.M.	15°.1	15°.6	42.63	9.78	9.40	0.38
11.00 P.M.	15°.0	15°.8	42.70	9.77	9.40	0.37
May 18.						
4.30 A.M.	15°.0	15°.8	42.67	9.77	9.40	0.37
				9.77	9.40	0.37

Molecular osmotic pressure, 24.43.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.039.

Table VIII.

o.4 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 47°.9; (2) at conclusion of expr., 47°.9; loss, o. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, o. Cell used, A₃. Resistance of membrane, 70,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 8.89. Time of setting up cell, 4.00 P.M., May 16, 1908.

Time.	Temperature.		Volume	Pressure.		
	Solution.	Manometer.	N₂.	Osmotic.	Gas.	Difference.
May 17.						
7.00 A.M.	15°.1	15°.8	46.53	9.77	9.40	0.37
12.00 M.	15°.0	15°.8	46.51	9.78	9.40	0.38
11.00 P.M.	15°.0	15°.8	46.52	9.77	9.40	0.37
May 18.						
4.30 A.M.	15°.0	15°.8	46.48	9.78	9.40	0.38
				9.78	9.40	0.38

Molecular osmotic pressure, 24.45.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.040.

Table IX.

0.5 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 58°.7; (2) at conclusion of expr., 58°.7; loss, o. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.51 mm. Cell used, A₃. Resistance of membrane, 26,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution; o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 10.47. Time of setting up cell, 4.00 P.M., Apr. 21, 1908.

Time. Apr. 21.	Temperature.		Volume N₂	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	15°.0	15°.3	32.06	(12.27)	11.75	(0.52)
Apr. 22.						
9.00 A.M.	15°.0	15°.1	32.03	12.29	11.75	0.54
12.00 M.	15°.0	15°.2	32.04	12.28	11.75	0.53
3.00 P.M.	15°.0	15°.4	31.99	12.30	11.75	0.55
				12.29	11.75	0.54

Molecular osmotic pressure, 24.58.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.046.

Table X.

0.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 58°.7; (2) at conclusion of expr., 58°.7; loss, o. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.09 mm. Cell used, B₃. Resistance of membrane, 122,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 10.19. Time of setting up cell, 4.30 P.M., May 12, 1908.

Time. May 13.	Temperature.		Volume. N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
8.30 A.M.	15°.0	16°.0	32.07	12.27	11.75	0.52
May 14.						
8.30 A.M.	15°.1	16°.1	31.99	12.30	11.75	0.55
3.00 P.M.	15°.1	16°.3	32.02	12.29	11.75	0.54
				12.29	11.75	0.54

Molecular osmotic pressure, 24.58.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.046.

Table XI.

0.6 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 69°.1; (2) at conclusion of expr., 69°.1; loss, 0. *Manometer:* No. 21; volume of nitrogen, 362.46; displacement, 0.18 mm. Cell used, G. Resistance of membrane, 121,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.70. Time of setting up cell, 4.30 P.M., Apr. 22, 1908.

Time. Apr. 23.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
4.30 P.M.	15°.0	15°.6	23.56	14.91	14.09	0.82
9.30 "	15°.0	15°.4	23.57	14.91	14.09	0.82
Apr. 24.						
8.30 A.M.	15°.0	15°.4	23.59	14.90	14.09	0.81
				14.91	14.09	0.82

Molecular osmotic pressure, 24.85.
Molecular gas pressure, 23.48.
Ratio of osmotic to gas pressure, 1.058.

Table XII.

0.6 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 69°.1; (2) at conclusion of expr., 69°.1; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.07 mm. Cell used, D. Resistance of membrane, 273,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.79. Time of setting up cell, 4.30 P.M., April 22, 1908.

Time. Apr. 23.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
4.30 P.M..	15°.0	15°.6	28.54	14.79	14.09	0.70
Apr. 24.						
8.30 A.M.	15°.0	15°.4	28.50	14.82	14.09	0.73
12.30 P.M.	15°.0	15°.6	28.52	14.81	14.09	0.72
				14.81	14.09	0.72

Molecular osmotic pressure, 24.68.
Molecular gas pressure, 23.48.
Ratio of osmotic to gas pressure, 1.051.

Table XIII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 79°.0; (2) at conclusion of expr., 78°.9; loss, 0°.10 = 0.13 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.02 mm. Cell used, A_3. Resistance of membrane, 56,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.59. Time of setting up cell, 3.00 P.M., May 20, 1908.

| Time. | Temperature. | | Volume N_2 | Pressure. | | |
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 21.						
3.00 P.M.	15°.0	15°.8	22.81	17.39	16.44	0.95
11.30 "	15°.0	16°.0	22.80	17.40	16.44	0.96
May 22.						
6.00 A.M..	15°.0	15°.7	22.80	17.40	16.44	0.96
10.00 "	15°.0	15°.9	22.80	17.40	16.44	0.96
				17.40	16.44	0.96

Molecular osmotic pressure, 24.86.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.058.

Table XIV.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 79°.0; (2) at conclusion of expr., 78°.95; loss, 0°.05 = 0.06 per cent. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.10 mm. Cell used, B_3. Resistance of membrane, 293,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.46. Time of setting up cell, 3.30 P.M., May 20, 1908.

| Time. | Temperature. | | Volume N_2 | Pressure. | | |
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 21.						
5.00 P.M.	15°.0	16°.0	26.65	17.35	16.44	0.91
May 22.						
6.00 A.M.	15°.0	15°.7	26.64	17.35	16.44	0.91
10.00 "	15°.0	15°.9	26.66	17.34	16.44	0.90
				17.35	16.44	0.91

Molecular osmotic pressure, 24.79.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.055.

Table XV.

0.8 Wt. normal solution.   Exp. No. 1.   *Rotation:* (1) original, 89°.05; (2) at conclusion of expr., 88°.85; loss, 0°.2 = 0.22 per cent.   *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.11 mm.   Cell used, G.   Resistance of membrane, 210,000.   *Corrections:* (1) atmospheric pressure, 1.0; (2) liquids in manometer, 0.60; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02.   Initial pressure, 16.19.   Time of setting up cell, 4.30 P.M., May 14, 1908.

Time.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 15.						
5.00 P.M.	15°.0	15°.6	21.18	20.04	18.79	1.25
May 16.						
3.30 A.M.	15°.0	15°.4	21.19	20.03	18.79	1.24
6.30 "	15°.0	15°.4	21.18	20.04	18.79	1.25
				20.04	18.79	1.25

Molecular osmotic pressure, 25.05.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 Wt. normal solution.   Exp. No. 2.   *Rotation:* (1) original, 88°.7; (2) at conclusion of expr., 88°.55; loss, 0°.15 = 0.17 per cent.   *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.26 mm.   Cell used, D.   Resistance of membrane, 263,000.   *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02.   Initial pressure, 13.66.   Time of setting up cell, 5.00 P.M., May 18, 1908.

Time.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 19.						
12.00 M.	15°.0	15°.8	21.14	20.09	18.79	1.30
11.00 P.M.	15°.0	15°.8	21.16	20.07	18.79	1.28
May 20.						
11.00 A.M.	15°.0	15°.7	21.12	20.11	18.79	1.32
				20.09	18.79	1.30

Molecular osmotic pressure, 25.11.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.069.

Table XVII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 98°.3; (2) at conclusion of expr., 98°.0; loss, 0°.3 = 0.31 per cent. *Manometer:* No. 15; volume of nitrogen, 419.63; displacement, 0.15 mm. Cell used, D. Resistance of membrane, 112,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.60; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.39. Time of setting up cell, 4.30 P.M., May 5, 1908.

Time. May 6.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
10.00 P.M.	15°.0	15°.0	18.00	22.90	21.14	1.76
May 8.						
8.30 A.M.	15°.0	15°.0	17.97	22.94	21.14	1.80
2.00 P.M.	15°.0	15°.3	17.99	22.92	21.14	1.78
				22.92	21.14	1.78

Molecular osmotic pressure, 25.47.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.084.

Table XVIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 97°.8; (2) at conclusion of expr., 97°.65; loss, 0°.15 = 0.15 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.13 mm. Cell used, G. Resistance of membrane, 210,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.64; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.21. Time of setting up cell, 5.00 P.M., May 18, 1908.

Time. May 19.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
4.30 P.M.	15°.0	15°.8	18.64	22.87	21.14	1.73
11.00 "	15°.0	15°.8	18.60	22.92	21.14	1.78
May 20.						
5.00 A.M.	15°.0	15°.6	18.64	22.87	21.14	1.73
12.00 M.	15°.0	15°.7	18.61	22.91	21.14	1.77
				22.89	21.14	1.75

Molecular osmotic pressure, 25.43.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.083.

Table XIX.

1.0 Wt. normal solution. Exp. No. 1.   *Rotation:* (1) original, 107°.5; (2) at conclusion of expr., 107°.5; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.33 mm. Cell used, D. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.88. Time of setting up cell, 4.00 P.M., Apr. 30, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 1.						
10.30 P.M.	15°.0	15°.1	16.82	25.38	23.49	1.89
May 2.						
12.30 P.M.	15°.0	15°.1	16.82	25.39	23.49	1.90
11.00 "	15°.0	14°.8	16.81	25.41	23.49	1.92
				25.39	23.49	1.90

Molecular osmotic pressure, 25.39.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.080.

Table XX.

1.0 Wt. normal solution. Exp. No. 2.   *Rotation:* (1) original, 107°.5; (2) at conclusion of expr., 107°.2; loss, 0°.3 = 0.28 per cent. *Manometer:* No. 15; volume of nitrogen, 419.63; displacement, 1.29 mm. Cell used, G. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.04; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.55. Time of setting up cell, 4.00 P.M., Apr. 3, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 2.						
12.30 P.M.	15°.0	15°.1	16.28	25.39	23.49	1.90
5.00 "	15°.0	15°.0	16.27	25.40	23.49	1.91
11.00 "	15°.0	14°.8	16.27	25.40	23.49	1.91
				25.40	23.49	1.91

Molecular osmotic pressure, 25.40.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.081.

Table XXI.—Summary of Results.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1 "	15°.0	0°.00	0.00	2.47	2.35	0.12	24.65	23.50	1.049
	15°.0	0°.00	0.00	2.48	2.35	0.13	24.83	23.50	1.056
0.2 "	14°.9	0°.10	0.01	4.91	4.70	0.21	24.55	23.50	1.044
	15°.0	0°.00	0.00	4.90	4.70	0.20	24.50	23.50	1.043
0.3 "	15°.1	0°.00	0.00	7.31	7.05	0.26	24.37	23.50	1.037
	15°.0	0°.00	0.00	7.35	7.05	0.30	24.50	23.50	1.043
0.4 "	15°.0	0°.00	0.00	9.77	9.40	0.37	24.43	23.50	1.039
	15°.0	0°.00	0.00	9.78	9.40	0.38	24.45	23.50	1.040
0.5 "	15°.0	0°.00	0.00	12.29	11.75	0.54	24.58	23.50	1.046
	15°.0	0°.00	0.00	12.29	11.75	0.54	24.58	23.50	1.046
0.6 "	15°.0	0°.00	0.00	14.91	14.09	0.82	24.85	23.48	1.058
	15°.0	0°.10	0.00	14.81	14.09	0.72	24.68	23.48	1.051
0.7 "	15°.0	0°.05	0.02	17.40	16.44	0.96	24.86	23.49	1.058
	15°.0	0°.20	0.01	17.35	16.44	0.91	24.79	23.49	1.055
0.8 "	15°.0	0°.15	0.03	20.04	18.79	1.25	25.05	23.49	1.067
	15°.0	0°.30	0.02	20.09	18.79	1.30	25.11	23.49	1.069
0.9 "	15°.0	0°.15	0.05	22.92	21.14	1.78	25.47	23.49	1.084
	15°.0	0°.00	0.02	22.89	21.14	1.75	25.43	23.49	1.083
1.0 "	15°.0	0°.30	0.00	25.39	23.49	1.90	25.39	23.49	1.080
	15°.0		0.04	25.40	23.49	1.91	25.40	23.49	1.081

Table XXII.—Summary of Results.   Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.
0.1	15°.00	0°.00	0.00	2.48	2.35	0.13
0.2	14°.95	0°.05	0.005	4.91	4.70	0.21
0.3	15°.05	0°.00	0.00	7.33	7.05	0.28
0.4	15°.00	0°.00	0.00	9.78	9.40	0.38
0.5	15°.00	0°.00	0.00	12.29	11.75	0.54
0.6	15°.00	0°.00	0.00	14.86	14.09	0.77
0.7	15°.00	0°.08	0.015	17.38	16.44	0.94
0.8	15°.00	0°.18	0.025	20.07	18.79	1.28
0.9	15°.00	0°.23	0.035	22.91	21.14	1.77
1.0	15°.00	0°.15	0.02	25.40	23.49	1.91

Concentration.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	24.74	23.50	1.053
0.2	24.53	23.50	1.044
0.3	24.44	23.50	1.040
0.4	24.44	23.50	1.040
0.5	24.58	23.50	1.046
0.6	24.77	23.48	1.055
0.7	24.83	23.49	1.057
0.8	25.08	23.49	1.068
0.9	25.45	23.49	1.084
1.0	25.40	23.49	1.081

It was stated in the paper[1] on the osmotic pressure of cane sugar solutions at 10° that a comparison of the pressures obtained at 0°, 5°, and 10° would reveal some evidence of a temperature coefficient, and that this fact would be further commented upon when we presented the results obtained at 15°. We can now say with considerable confidence that the osmotic pressure of cane sugar solutions, between 5° and 15°, not only exhibits a temperature coefficient, but one which is practically identical with the temperature coefficient of gases.

Table XXIII. gives the pressures which have been obtained at 0°, 5° (more precisely, between 4° and 5°), 10°, and 15°, and it will be made the basis of the discusssion which follows. The results are presented *without correction for loss in rotation.* They are, in other words, the *observed pressures*, and

[1] This Journal, **39**, 667.

Table XXIII.—Osmotic Pressure. Series III.–VI.

Concentration.	Series III. Pressures. 0°.		Series IV. Pressures. 4°–5°.		Series V. Pressures. 10°.		Series VI. Pressures. 15°.
0.1	2.42		2.40		2.44		2.48
0.2	4.79		4.75		4.82		4.91
0.3	7.11		7.07		7.19		7.33
0.4	9.35		9.43		9.58		9.78
0.5	11.75		11.82		12.00		12.29
0.6	14.12		14.43		14.54		14.86
0.6	16.68		16.79		17.09		17.39
0.7	19.15		19.31		19.75		20.09
0.8	21.89		22.15		22.28		22.94
0.9	24.45		24.53		25.06		25.42
1.0							
1 Total pressures	131.71		132.68		134.75		137.49
2 Differences		0.97		2.07		2.74	
3 Mean molecular osmotic pressures	23.95		24.12		24.50		24.98
4 Differences		0.17		0.38		0.48	
5 Mean molecular gas pressures	22.29		22.65		23.09		23.50
6 Differences		0.36		0.44		0.41	
7 Mean ratio of osmotic to gas pressure	1.074		1.065		1.061		1.064
8 Mean loss in rotation (per cent)	1.73		1.45		0.22		0.10

they are, in our judgment, very nearly correct. The reasons for discontinuing the correction of the observed pressures for the loss in rotation which the solutions suffered while in the cells have been given in former papers in some detail, but a recapitulation of them here may not be superfluous. In the first place, we have long observed that duplicate determinations, which differed considerably in respect to loss in rotation, agreed better before than after correction, indicating that the major portion of the dilution of the solutions occurred *after* the measurement of pressure, *i. e.*, while the cells were being opened. This view of the case was strengthened by the fact that, while the cells are being opened, the contents are much of the time under diminished pressure, which necessarily facilitates the entrance of water from the cell wall. Again, it was found that the loss in rotation was considerably diminished by the practice of dipping the cells, just before opening them, in a sugar solution whose concentration was equal to, or slightly greater than, that of the solution within the cell. The final proof that practically all loss in rotation was subsequent to the measurement of pressure, and therefore negligible, came when it was found that, if the dilution occurring during the opening of the cell is suppressed, the loss in rotation becomes insignificant. It then became apparent that the *observed* pressures are the correct ones, and that our earlier practice of correcting for loss in rotation as inversion or dilution, or both, was wrong. This conclusion applies strictly to all measurements which were made after the displacement of the manometers and the distortion of the stoppers had been brought under control, but only partially to the earlier ones; that is, it applies to Series III. at 0°, and to Series IV. at temperatures between 4° and 5°, but not to Series I. and II. at temperatures between 20° and 25°. We therefore consider ourselves justified in introducing into Table XXIII. the actually observed pressures of Series III. and IV., and in omitting Series I. and II., which are already undergoing revision. A few words of explanation will be given for each of the series in Table XXIII.

Series III. at 0°.—The temperature at which this series of

measurements was made ranged from 0°.12 to 0°.38. The *thermometer effects* were small as compared with those of earlier series, as were also the dilution effects due to displacements of manometers and distortions of stoppers. Nevertheless, it is expected that the values given in the table will be somewhat modified when the work is repeated. The changes will not be large, and in most cases they will probably not extend beyond the second decimal place. It will be noted (line 8) that the average loss in rotation in this series amounted to 1.73 per cent, which is very large when compared with the losses in Series V. and VI. It has already been explained, however, that by far the greater portion of this loss was due to the diminished pressure which prevailed while the cells were being opened, and that it does not, therefore, affect the accuracy of the measurements of pressure.

Series IV.—The measurements here were obtained under much the same conditions as those of Series III. The temperature of the bath, however, was regulated at that time by running water alone, and not, as now, by running water and automatically controlled electric stoves. The bath temperatures ranged from 4°.32 to 6°.05, but were generally between 4° and 5°. When the work is repeated, the bath will be maintained at 5°. The thermometer effects were probably somewhat greater than in Series III., but not large enough to affect seriously the accuracy of the results. The dilution, as indicated by the loss in rotation (line 8), was less than in Series III. The values given in Table XXIII. for this series will probably not be greatly modified through revision.

Series V. and VI.—The work at 10° and 15° was carried out under much better conditions than that at the lower temperatures. The control of temperature had been perfected to a point where thermometer effects were no longer unavoidable. Improved methods of calibrating, comparing, and testing the manometers had been introduced, and the manometers were filled with nitrogen instead of air. The cells used in a part of the determinations were of a new pattern, which made it possible to eliminate certain small errors which could not be avoided in the earlier work. But, more important than all

the improvements thus far enumerated, was the discovery of the means by which practically all the dilution of the cell contents can be suppressed. The extent of the improvement in this particular can be seen in line 8 of Table XXIII., where the losses in rotation recorded for Series V. and VI. are 0.22 per cent and 0.10 per cent, respectively. In our judgment, the errors of both series are limited to the second decimal place of the numbers expressing the osmotic pressures.

In comparing Series III., IV., V., and VI. with a view to discovering evidences of a temperature coefficient, it is better to consider each series as a unit, and this has been done in Table XXIII. By so doing, certain discrepancies observable among the individual concentrations are kept from obscuring the general trend of the values. We do not mean that such local discrepancies in the table are to be ignored; on the contrary, each one of them will be carefully investigated.

If the totals of the number of atmospheres measured in each series are compared (Table XXIII., line 1), it will be seen that they increase with rising temperature (line 2), the increase from Series III. to IV. being 0.97 atmosphere, from IV. to V., 2.07 atmospheres, and from V. to VI., 2.74 atmospheres. It is to be remembered that the temperature intervals are not quite equal. Between III. and IV. it is somewhat less than 5 degrees, and between IV. and V. it is somewhat more than 5 degrees, while between V. and VI. the temperature interval is exactly 5 degrees.

In line 3 of the table, the molecular osmotic pressure of each series, considered as a unit, is given. They are obtained, of course, by dividing the total pressure (line 1) by 5.5, the sum of the weight normal concentrations by tenths. The molecular osmotic pressure increases from 23.95 atmospheres (Series III.) to 24.98 atmospheres (Series VI.), but the various increments (line 4) are not strictly proportional to the temperature intervals. The increase in molecular osmotic pressure between 0° (Series III.) and 4°–5° (Series IV.) appears to be relatively much smaller than between 4°–5° (Series IV.) and 10° (Series V.), and also smaller than between 10° (Series V.) and 15° (Series VI.). The plain inference from this rela-

tion is that the temperature coefficient of osmotic pressure is smaller below the temperature of maximum density of the solvent than above it; but the suggestion is to be received with caution, because the values in Series III. and IV. are not so well established as are those of Series V. and VI., and a revision of them may alter the relation in question. The temperature interval between Series IV. and V. is longer than between Series V. and VI., but the increment in molecular osmotic pressure is smaller—0.38 atmosphere against 0.48 atmosphere. This suggests the possibility that the temperature coefficient of osmotic pressure increases with rising temperature; but here again some caution is called for, because a redetermination of the osmotic pressure at 5° may modify the value 0.38.

For the purpose of comparing osmotic with gas pressure with respect to the effect of rising temperature, the molecular gas pressures, corresponding to the molecular osmotic pressures, are given in line 5 of the table, and their differences in line 6. It will be seen that while osmotic pressure increases 1.03 atmospheres between 0° and 15°, gas pressure increases 1.21 atmospheres. *But if we consider the interval between 4°–5° (Series IV.) and 15° (Series VI.) the increase in osmotic pressure is almost identical with that of gas pressure, the increments in question being 0.86 atmosphere and 0.85 atmosphere, respectively.* There is in these relations strong evidence that, between 5° and 15°, the osmotic pressures of *weight normal* solutions of cane sugar obey the law of Gay-Lussac for gases.

There is presented in line 7 of the table another phase of the relations of osmotic to gas pressures namely, the ratios of the two for the different series. If the temperature coefficients of osmotic and gas pressure are equal between 5° and 15°, these ratios should be equal. They are 1.065, 1.061, and 1.064, and are probably to be regarded as substantially equal, since very slight changes in the totals (line 1) of the osmotic pressure of Series IV., V., and VI. would cause the differences between them to disappear.

The form of statement adopted for Table XXIII. appears to be a good one for the general presentation of the results of

past work, and the table will reappear from time to time—enlarged and probably somewhat amended also—as the experimental data accumulate. We are now engaged in measuring the osmotic pressure of cane sugar solutions at 20°, 25°, and 30°, with a view to ascertaining whether at higher temperatures the ratio of osmotic to gas pressure in these solutions drops from 1.06 (5°, 10°, and 15°) to unity.

Johns Hopkins University,
May 25, 1908.

REVIEWS.

Organic Chemistry for Advanced Students. By Julius B. Cohen, Ph.D., B.Sc. New York: Longmans, Green & Co.; London: Edward Arnold. 1907. pp. viii + 632. Price, $7.

This excellent book should be read by all advanced students and teachers of chemistry. As the author tells us in the preface, the volume is a compilation of his lectures to advanced students in organic chemistry; a mass of interesting facts is given, and the treatment of the subject recalls to the reviewer the flavor of Lachmann's "Spirit of Organic Chemistry." One of the most important features of the book is the very complete list of references to the literature, a point overlooked too often by writers of English texts.

After an excellent historical introduction giving the development of the radical theory, type theory, and others, up to the present time, the author takes up special chapters of importance, and treats each with a thoroughness that is rare.

In Chapters II, III, and IV, the author takes up the stereo-isomerism of carbon and nitrogen compounds, as illustrated in sugars, oximes, hydrazones, maleic acid, etc.; all that could be desired in addition is, perhaps, a full account of Rosanoff's work on optical superposition and a discussion of sterical hindrance in optically active cyclic compounds along the lines discussed by van't Hoff, Skraup, and Jacobson .[1] One or two small errors have crept into this chapter, as in others. For instance, the author tells us on page 157 that the α and β compounds obtained by Marckwald by the action of mustard oils on hydrazines are stereoisomeric forms of 1,4-dialkylthio-semicarbazides. These have been proved by the work of Busch especially to be 1,4- and 2,4-dialkylthiosemicarbazides. On page 185 we are told that tautomeric amidines and hydraz-amidines have been isolated by von Pechmann and Walther.

[1] Ber. d. chem. Ges., **35**, 3981, 3984.

Wheeler has shown that such tautomerism does not exist in any known compounds; that Walther's tautomeric amidines were impure samples of the same compound, and that von Pechmann's tautomeric hydrazamidines are structural isomers.

Chapter V, on Isomeric Change, including Tautomerism, is the best one ever written on this subject. The author might have added the recent quantitative work on the reactions of tautomeric salts with alkyl halides.

Chapter VII gives an excellent account of the syntheses by the methods of Wurtz, Fittig, Wislicenus, Perkin, Frankland, Grignard, and of the acetoacetic ester and analogous condensations.

The chapter on Carbohydrates and the chapters on Fermentation, the Purine Group, and the Proteins, for aid in which the author is indebted to Dr. H. D. Dakin, are very full.

The otherwise excellent chapter on the Benzene Theory does not present the recent work of Pope and Barlow on the relation of chemical constitution and crystallographic properties. There is a very good chapter on Terpenes, in which the author gives the important syntheses and a good table of the natural essential oils and their constituents.

Chapter XIV gives an excellent account of the alkaloids derived from quinoline, pyrrolidine, and pyridine, etc., including even the recent work of Pschorr, Knorr, and Vongerichten on the morphine bases, and of the late Koenigs on the quinine bases.

A chapter on Dyestuffs would make this excellent book well-nigh complete. S. F. ACREE.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemischer Betriebe, für Handel und Unterricht. Herausgegeben von PROF. DR. BERNARD NEUMANN, Grossherzogliche technische Hochschule, Darmstadt. Dritte, vermehrte und verbesserte Auflage. Erster Band, Viertes Heft. Braunschweig: Vieweg u. Sohn. 1908. pp. 815–974. Price, unbound, M.4.20.

This section of this well-known work comprises the chapters upon the Inorganic Acids, by Dr. H. Benedict; on Soda, by Dr. W. Kolb; on Potassium Salts and on Bromine, by Dr. Bokemüller; on Potash and Saltpeter, by Dr. E. Schafer; and on Sodium Sulphide, Sodium Thiosulphate, Alumina, and Aluminium Sulphate, also by Dr. Kolb. This completes the first volume of the work and the necessary tables of contents, title pages, etc., accompany this section. The character of the work is well maintained in these chapters, and they, like those which have already appeared, deserve the careful attention of analysts. H. P. TALBOT.

As the title implies, this monograph is a record of the English patents in the field of electrochemistry. It covers the field from 1842 to 1906, and will doubtless prove of great service to all who are interested in technical electrochemistry.   H. C. J.

This volume covers the field of analysis and testing of mixed paints, color pigments, and their vehicles better than any book yet published on this subject. It will be of value to the engineer as well as the analyst and will be an aid in preparing specifications for paints and painting.

The opening chapter by Professor Ladd clearly shows, from his analysis of ready mixed paints, the necessity of some form of paint legislation. False statement regarding composition, oils emulsified with water, and short measure are gross adulterations which demand correction. The main features of the North Dakota Paint Law are stated and show the measures adopted to remedy this condition. Till, however, the so-called statutory pigments (white lead and white zinc) are proved to be superior to the reinforced pigments under all conditions of service, both should be labeled in the same manner. Professor Ladd's position appears to discriminate in favor of the statutory pigments. The elaborate series of service tests started in various sections of the country since the North Dakota Paint Law went into effect will undoubtedly throw some light on this subject and open the way to further tests which will clearly demonstrate the points at issue.

The main portion of the volume is prepared by Dr. Holley. His association with Professor Ladd while the paint legislation was prepared gives an added value to the volume. The analytical data are very complete, covering sampling, separation of pigment from vehicle, with full scheme of analysis for each portion. The chapters on vehicles and volatile oils include

most of the tests used by commercial paint chemists, beside giving the general methods of oil analysis as found in the standard works on this subject. The data on analysis of pigments will be of value to the analyst, though a few of the schemes for the analysis of complex white pigments containing lead, zinc, lime, and barium in several combinations may require verification. The chapters on the physical and practical testing of paints are of the most value to the paint chemist and should always supplement the chemical analysis. The analysis and practical testing of driers and Japans gives a means to determine the value of these materials. The chapter on varnish analysis, gives all the information available on this complex subject, but unfortunately the data obtained by chemical analysis do not fully demonstrate the value of this product, so physical and practical tests are even more necessary in this case than in testing out paint.

A standardization of these practical tests to measure the physical constants of the film is much to be desired.

Altogether this volume will be welcomed by all technical chemists. S. S. VOORHEES.

ERRATA IN THE TABLE OF CONTENTS AND INDEX OF
VOLUME 39.

AMERICAN

CHEMICAL JOURNAL

TRIPHENYLINDENE AND SOME OF ITS DERIVATIVES.

By E. P. Kohler.

In an earlier paper[1] I described the preparation of diphenyl-benzalacetophenone by boiling α-bromtriphenylpropiophenone with a strong alcoholic solution of potassium hydroxide:

$$(C_6H_5)_2CHCBr(C_6H_5)COC_6H_5 + KOH =$$
$$(C_6H_5)_2C : C(C_6H_5)COC_6H_5 + KBr + H_2O.$$
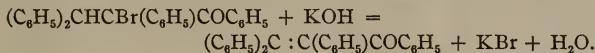
This procedure invariably gives, in addition to the unsaturated ketone, a small quantity of a substance that separates from solution in large colorless crystals and has a melting point that is considerably higher than that of the ketone. The filtrate from a number of preparations of unsaturated ketone yielded a sufficient quantity of this substance for an analysis and a determination of its molecular weight. The results are expressed by the formula $C_{29}H_{24}O$.

A compound having the composition $C_{29}H_{24}O$ might be formed by addition of alcohol to the unsaturated ketone and loss of water from the product, but an experiment showed that the ketone is not affected by prolonged boiling with alcoholic

[1] This Journal, **38**, 559.

potassium hydroxide. The substance must, therefore, be formed from the bromoketone—either by replacement of bromine with ethoxyl and subsequent elimination of water or, *vice versa*, by loss of water succeeded by replacement of bromine.

By keeping an alcoholic solution of α-bromtriphenylpropiophenone at a low temperature for a long time it is possible to replace bromine with ethoxyl. Not a trace of the compound $C_{29}H_{24}O$ is formed under these conditions and I have found no way of getting this substance from the ethoxyketone. It is, however, easy to eliminate water from the bromoketone. When it is heated either by itself or in solution in indifferent solvents it loses one molecule of water and passes almost quantitatively into the bromide $C_{27}H_{19}Br$. When the bromide is dissolved in alcohol it gives the compound $C_{29}H_{24}O$. This is, therefore, an ether formed from α-bromtriphenylpropiophenone in accordance with the equations

I. $(C_6H_5)_2CHCBr(C_6H_5)COC_6H_5 — H_2O = C_{27}H_{19}Br$;
II. $C_{27}H_{19}Br + C_2H_5OH = C_{27}H_{19}OC_2H_5 + HBr$.
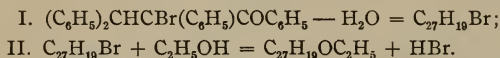
The structure of the ether was established by the following transformations: Both the bromide and the ether are readily oxidized with chromic acid dissolved in acetic acid. The principal oxidation products are in each case benzoic acid and *o*-dibenzoylbenzene. The formation of the latter in this reaction indicates the presence of a condensed ring system containing one benzene ring and shows the position of two of the phenyl groups. In order to establish the character of the second ring and to locate the remaining groups it was necessary to introduce a hydrocarbon residue in place of bromine or ethoxyl. This was accomplished with ethylmagnesium bromide which reacts with the bromide in accordance with the equation

$$C_{27}H_{19}Br + C_2H_5MgBr = C_{27}H_{19}C_2H_5 + MgBr_2.$$
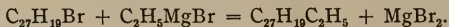
The hydrocarbon resulting from this reaction gives only one product when oxidized with chromic acid at the ordinary temperature—a diketone with all the hydrocarbon residues intact. On further oxidation in boiling acetic acid, the dike-

tone gives *o*-dibenzoylbenzene. These results show that the hydrocarbon is a derivative of 1,2,3-triphenylindene:

$$C_6H_5 \quad C_6H_5$$

(structures omitted)
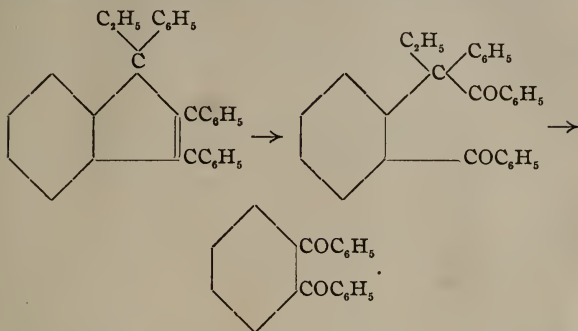
The bromide $C_{27}H_{29}Br$ is therefore 1-brom-1,2,3-triphenylindene and it is evident that there must be a shifting of the bromine atom when α-bromtriphenylpropiophenone loses water and passes into the indene derivative:

$$(C_6H_5)_2CHCBr(C_6H_5)COC_6H_5 =$$

(structures omitted)
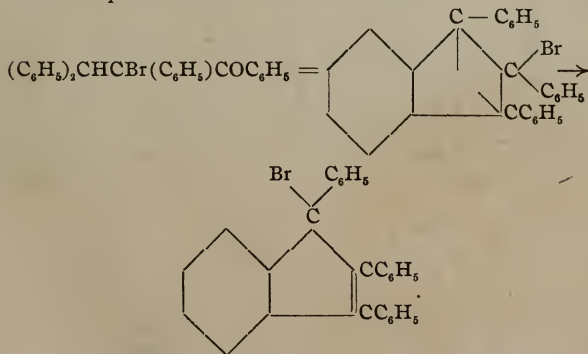
It is remarkable that a change so complicated as this one should take place far below the melting point of the bromoketone, and without more than a trace of by-products. I have made a number of experiments for the purpose of determining

to what extent this reaction can be used for making other indene derivatives and have found that the reaction does not take place either with the ketone that has hydrogen in place of bromine, or with bromoketones that have hydrogen or alkyl in place of any of the phenyl groups in bromtriphenylpropiophenone.

By starting with bromtriphenylindene it is easy to get triphenylindene itself as well as a number of derivatives that are of interest in connection with recent investigations of substances that are rich in phenyl groups. The hydrocarbon behaves almost exactly like triphenylmethane. The single hydrogen atom attached to the indene ring is readily replaced both by halogens and by potassium. The hydrocarbon can be oxidized directly to the carbinol. The halogen substitution products are slightly less reactive than the corresponding triphenylmethane derivatives but give the characteristic reactions of those substances. Thus the yellow bromide forms double salts with metallic halides, reacts with alcohols to form ethers, and gives, with metals, an unsaturated compound analogous to "triphenylmethyl." Similarly, the carbinol obtained by replacing bromine with hydroxyl gives the typical color and condensation reactions of triphenylcarbinol.

The only phenyl substitution product of indene hitherto described is a substance obtained by Vorländer and Siebert[1] by molecular rearrangement of tetraphenylallene. Vorländer and Siebert showed that the structure of their hydrocarbon must be totally different from that of tetraphenylallene and

suggested the formula
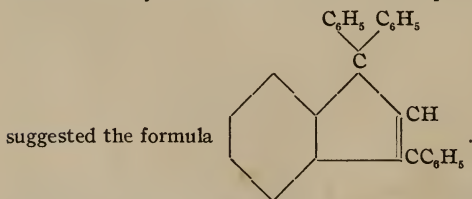
As the substance has the same melting point as the triphenylindene described in this paper and as the oxidation products

[1] Ber. d. chem. Ges., **39,** 1030.

obtained by heating the two hydrocarbons with chromic acid in acetic acid also melt at the same temperature, it was necessary to repeat the experiments with tetraphenylallene. The results show that the substances are different and that the formula proposed by Vorländer and Siebert is correct. By cautious oxidation it is possible to convert their hydrocarbon into a ketonic acid that readily loses carbon dioxide and that can be oxidized to *o*-dibenzoylbenzene:
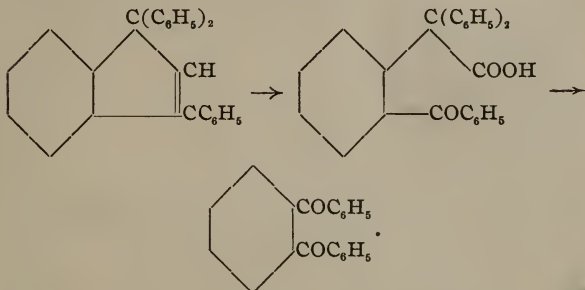
The behavior of this hydrocarbon is quite different from that of 1,2,3-triphenylindene; it cannot be oxidized to the carbinol, it has no hydrogen that is replaceable by metals, the bromine substitution product is colorless, and the bromine is not available for metathetical reactions.

EXPERIMENTAL PART.

Preparation of Bromtriphenylpropiophenone.—As triphenyl-propiophenone does not react with bromine[1] it is necessary to make the bromine substitution product indirectly, by the action of bromine on the magnesium derivative obtained as a result of adding phenylmagnesium bromide to benzalde-oxybenzoin.[2] Even this method gives very poor yields unless special precautions are taken to avoid rise in temperature during the addition of bromine and while isolating the product. The following procedure gives satisfactory results:

[1] THIS JOURNAL, **34**, 572.
[2] *Ibid.*, **36**, 195.

One hundred grams of finely powdered benzaldeoxybenzoin is added in small quantities to an ethereal solution of phenylmagnesium bromide made from 20 grams of magnesium. The solution is boiled for a few minutes, then cooled with an efficient freezing mixture, and treated with 120 grams of bromine that has been dried by distillation from phosphorus pentoxide. The bromine should be added as slowly as possible from a dropping funnel that delivers very small drops and the mixture must be shaken constantly to avoid local rise in temperature. As soon as all the bromine has been added, the liquid is poured into a freezing mixture of ice and concentrated hydrochloric acid, contained in a separating funnel, shaken until the solid product begins to separate, then diluted with 2 to 3 times its volume of low-boiling ligroin that has been cooled in a freezing mixture.

By constant and vigorous shaking for an hour it is possible to get almost the entire product in the form of a fine crystalline deposit. After filtration this is washed—first with water, then with a mixture of ether and ligroin (1 to 4), and finally with low-boiling ligroin. The colorless powder left after drying over sulphuric acid in a vacuum contains small quantities of triphenylpropiophenone and tetraphenylpropenone. These substances may be removed by recrystallization from a mixture of chloroform and ligroin but for most purposes the carefully washed and dried product is sufficiently pure. The yield is satisfactory—120 to 140 grams from 100 grams of benzaldeoxybenzoin. By evaporating the filtrate and boiling the oily residue with alcoholic potassium hydroxide the bromoketone left in solution can be transformed into the sparingly soluble triphenylpropenone.

1-Brom-1,2,3-triphenylindene,

$CBrC_6H_5$

CC_6H_5
CC_6H_5
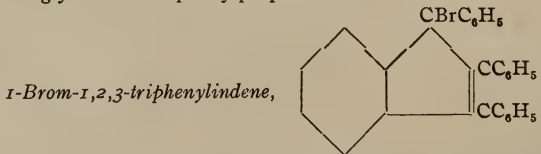
When bromtriphenylpropiophenone is heated in a capillary tube it melts at 124° and immediately decomposes with evolution

of gas, leaving an oily residue that is orange when hot, yellow when cold. The same decomposition takes place slowly when a clear, colorless crystal is heated on a steam bath. The crystal first turns yellow, then melts to a pale yellow liquid that gradually becomes darker in color and finally solidifies after heating for 50 to 60 hours. At the ordinary temperature the solid ketone seems to be stable but its solutions in indifferent solvents slowly turn yellow. A saturated solution of 10 grams in absolute ether, to which a small piece of fused calcium chloride had been added for the purpose of removing any water liberated, deposited 0.75 gram of bromide in 7 months. The same product was obtained in all these experiments—a yellow solid melting at 129°. To prepare this substance in quantity 50 gram portions of the bromoketone were heated for a short time to 150°–160° in wide beakers. The orange colored oil was poured, while hot, into a small quantity of boiling chloroform, the solution diluted with 0.5 volume of acetone and 4 to 5 volumes of ligroin (40°), and cooled in a freezing mixture. The product separated in minute yellow plates melting at 127°. To get a perfectly pure product it is best to recrystallize the substance from alcohol-free ether, from which it separates in large transparent plates melting at 129°.

Analysis:

I. 0.1198 grams ubstance gave 0.3373 gram CO_2 and 0.0485 gram H_2O.

II. 0.1319 gram substance gave 0.3700 gram CO_2 and 0.0534 gram H_2O.

	Calculated for $C_{27}H_{19}Br$.	Found. I.	II.
C	76.6	76.9	76.5
H	4.5	4.5	4.5

Bromtriphenylindene is stable in the air. It is readily soluble in chloroform and carbon tetrachloride, moderately in acetone and ethyl acetate, sparingly in ether and ligroin. It reacts rapidly with alcohol and it is slowly reduced by acetone. Pure cold sulphuric acid dissolves it only slightly while the hot acid decomposes it, forming hydrobromic acid

and an intensely red solution that gives the carbinol when diluted with water. The solution in liquid sulphur dioxide has the same color as the solid but readily gives metathetical reactions with salts. Thus dry silver sulphate reacts instantaneously, forming the calculated amount of silver bromide and a brilliant red sulphate. By using a very dilute solution it was possible to get the sulphate free from bromide, but the substance is so extremely sensitive to moisture that I failed to get consistent analytical results.

Bromtriphenylindene, like triphenylmethyl chloride, forms double salts with metallic halides. The dark red crystalline compound with aluminium bromide obtained by bringing the components together in nitrobenzene was analyzed.

I. 0.2011 gram substance gave 0.2191 gram AgBr.
II. 0.2504 gram substance gave 0.0188 gram Al_2O_3.

	Calculated for $C_{27}H_{19}Br.AlBr_3$.	I.	II.
Br	46.4	46.3	..
Al	3.8	....	4

Oxytriphenylindene,
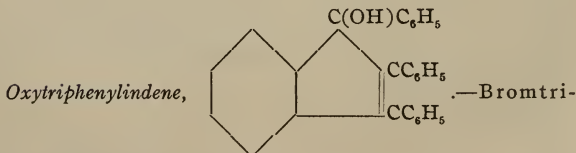
.—Bromtri-

phenylindene can be boiled with water and even with strong aqueous potassium hydroxide without undergoing appreciable change, but water or sodium acetate rapidly decolorizes the yellow solution in hot acetic acid. In each case bromine is replaced with hydroxyl. When the colorless solution is poured on ice the carbinol separates as a paste, which slowly passes into an amorphous solid. This can be filtered and washed but it is extremely difficult to get it in crystalline form as all the common solvents deposit it as an oil. The best results were obtained by dissolving it in glacial acetic acid, diluting the solution with water until a slight cloudiness appeared, redissolving this precipitate with a few drops of acetic acid,

and allowing the solution to evaporate spontaneously. In the course of a few weeks most of the substance separated in lustrous prisms that melt sharply at 129°.

Analysis:

0.1110 gram substance gave 0.3670 gram CO_2 and 0.0522 gram H_2O.

	Calculated for $C_{27}H_{20}O$.	Found.
C	90.0	90.2
H	5.5	5.3

Oxytriphenylindene is readily soluble in all common solvents except water and low-boiling ligroin. It also dissolves readily in cold concentrated sulphuric acid. The solution has an intensely red color which persists on heating. The carbinol does not react with boiling acetyl chloride and no acetyl derivative was obtained by prolonged boiling with acetic anhydride and sodium acetate. The presence of the hydroxyl group is shown by the behavior towards ethylmagnesium bromide. It liberates an equivalent quantity of ethane and is recovered unchanged when the resulting magnesium derivative is decomposed with water.

The *ethers* of oxytriphenylindene are very easily obtained by adding a few drops of concentrated sulphuric acid to its solutions in alcohols and boiling for a short time or by simply dissolving bromtriphenylindene in the boiling alcohols. As they are sparingly soluble in alcohol and crystallize well they served as a convenient means of detecting the carbinol in reaction products.

The *methyl ether, methoxytriphenylindene,* $C_{28}H_{22}O$, crystallizes in tables melting at 153°. Its solubility in various solvents and its behavior towards reagents are similar to those of the ethyl ether described below.

Analysis:

0.1422 gram substance gave 0.4667 gram CO_2 and 0.0788 gram H_2O.

	Calculated for $C_{28}H_{22}O$.	Found.
C	89.8	89.5
H	5.9	6.1

The *ethyl ether*, $C_{29}H_{24}O$, is readily soluble in chloroform and ethyl acetate, moderately in acetone and boiling ether, sparingly in alcohol and ligroin. It separates from acetone in large lustrous prisms melting at 172°.

Analysis:

I. 0.1100 grams ubstance gave 0.3630 gram CO_2 and 0.0627 gram H_2O.

II. 0.1278 gram substance gave 0.4202 gram CO_2 and 0.0725 gram H_2O.

	Calculated for $C_{29}H_{24}O$.	Found. I.	II.
C	89.7	90.0	89.6
H	6.2	6.4	6.3

The molecular weight was determined in boiling acetone. K = 1710.

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
36.40	0.6210	0.078	370
36.40	1.2550	0.160	366
36.40	1.9115	0.238	378

Calculated for $C_{29}H_{24}O$, 388

The ether does not reduce potassium permanganate dissolved in acetone but it is readily oxidized with chromic acid dissolved in hot glacial acetic acid. Ten grams of the substance were dissolved in 100 grams of boiling acetic acid and treated with small quantities of chromic acid until a permanent color of the acid remained in the liquid. The solution was then poured on ice and allowed to stand until the precipitated paste solidified. The solid was washed with water, dried, and crystallized from a mixture of acetone and alcohol. It separated in colorless tables melting at 148°.

Analysis:

I. 0.1189 gram substance gave 0.3649 gram CO_2 and 0.0525 gram H_2O.

II. 0.1321 gram substance gave 0.4055 gram CO_2 and 0.0584 gram H_2O.

	Calculated for $C_{20}H_{14}O_2$.	Found. I.	II.
C	83.9	83.7	83.7
H	4.9	4.9	5.0

The oxidation product has the composition of *o*-dibenzoyl-benzene, but this, according to Zincke, is pale yellow in color and melts at 146°. For the purpose of comparison I made *o*-dibenzoylbenzene by oxidizing *o*-dibenzylbenzene with chromic acid. The difficulties experienced by Zincke and by Wehnen in preparing this ketone can be obviated by using an aqueous solution of chromic acid. Ten grams of dibenzyl-benzene were dissolved in 100 cc. of boiling glacial acetic acid contained in a flask connected with an inverted condenser. A solution of 10 grams of chromic acid in the minimum quantity of cold water was added drop by drop from a funnel connected with the top of the condenser. The mixture was boiled until the color of chromic acid had disappeared, then poured into water, and the products separated in the usual way. The yield was 8 grams. By recrystallization from acetone and alcohol it was obtained in colorless tables that melted at 148°. A mixture of *o*-dibenzoylbenzene and the oxidation product obtained from ethoxytriphenylindene melted at the same temperature.

1-Ethyl-1,2,3-triphenylindene,

This substance was made in the hope of getting an oxidation product intermediate between the indene derivative and *o*-dibenzoylbenzene. It was easily obtained by adding bromtri-phenylindene to excess of ethereal ethylmagnesium bromide and boiling until the resulting solution was colorless. The product was isolated in the usual way and purified by recrystallization from acetone and alcohol. It was thus obtained in plates melting at 108°.

Analysis:

0.1125 gram substance gave 0.3860 gram CO_2 and 0.5645 gram H_2O.

	Calculated for $C_{29}H_{24}$.	Found.
C	93.55	93.6
H	6.45	6.6

The hydrocarbon is readily soluble in chloroform and acetone, moderately in alcohol and ether, sparingly in ligroin. It separates very slowly from solution but forms large and well-defined crystals. The yield was 13 grams from 15 grams of the bromide.

Benzoyltriphenylbutyrophenone,

$C_6H_5COC_6H_4C(C_2H_5)(C_6H_5)COC_6H_5$.—Ethyltriphenylindene does not reduce potassium permanganate dissolved in acetone. It was oxidized by adding chromic acid in small quantities to a cold solution in acetic acid as long as the color rapidly changed to green after each addition. The solution was then poured into ice water which precipitated a paste that remained liquid for a long time but solidified when rubbed in contact with ether. The solid was purified by crystallization from acetone. Yield of pure product, 10.2 grams.

Analysis:

I. 0.1190 gram substance gave 0.3732 gram CO_2 and 0.0635 gram H_2O.

II. 0.1314 gram substance gave 0.4147 gram CO_2 and 0.0706 gram H_2O.

	Calculated for $C_{29}H_{24}O_2$.	Found. I.	II.
C	86.1	85.5	86.0
H	5.9	5.9	5.9

Benzoyldiphenylbutyrophenone crystallizes in large shining tables melting at 180°. It is readily soluble in chloroform and acetone, sparingly in alcohol and ether. When boiled with excess of chromic acid in acetic acid it is slowly oxidized to *o*-dibenzoylbenzene and *o*-benzoylbenzoic acid.

Triphenylindenyl Peroxide, $C_{27}H_{19}O$—$OC_{27}H_{19}$.—It seemed probable, in view of the close resemblance between the substances described above and the corresponding derivatives of triphenylmethane, that it would be possible to eliminate bromine from the indene derivative and get a compound

analogous to "triphenylmethyl." This is the case. When the yellow solution of the bromide in dry benzene is shaken with mercury or, better, with amalgamated zinc, it rapidly changes in color from yellow to orange or red and, in case zinc amalgam is used, a thin film of a bright red double salt with zinc bromide forms on the metal. The double salt disappears after a time but the color of the solution is permanent. When the colored solution is allowed to evaporate in contact with dry air the color soon fades and a colorless crystalline deposit forms on the sides of the vessel. This is the peroxide. It was purified by recrystallization from a mixture of chloroform and ether.

Analysis:

0.1310 gram substance gave 0.4337 gram CO_2 and 0.0650 gram H_2O.

	Calculated for $(C_{27}H_{19}O)_2$.	Found.
C	90.25	90.3
H	5.57	5.4

The peroxide was obtained in small shining prisms that decompose at about 155°. It is readily soluble in chloroform, sparingly in acetone, alcohol, and ether. Its solution in sulphuric acid has the same color as that of the carbinol in the same solvent. From this solution water precipitates some carbinol while alcohol gives almost the calculated quantity of ethoxytriphenylindene.
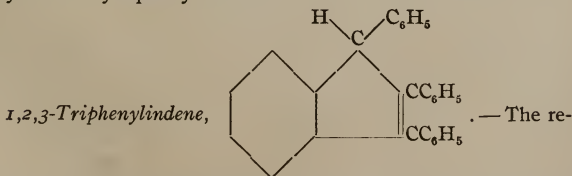
1,2,3-Triphenylindene, . — The results of the preceding experiment show that metals eliminate halogen from the bromide and form an unsaturated compound. This was utilized for passing from the halogen derivative to the hydrocarbon. In the presence of a small quantity of iodine magnesium reacts very readily with an ethereal solution of

the bromide but, apparently, without forming a trace of magnesium derivative. The experimental conditions were varied in every manner suggested by the results obtained by Schmidlin and by Tschitschibabin with triphenylchlormethane, but no magnesium derivative could be detected in the solution.

When the unsaturated compound, contained in the dark red solution obtained with magnesium, is oxidized with air or oxygen it gives almost the calculated amount of peroxide. When it is treated with water it gives approximately equal weights of triphenylindene and oxytriphenylindene. And when it is reduced it gives almost exclusively triphenylindene. The reduction was carried out as follows: Ten grams of the finely powdered halogen compound were suspended in 75 cc. of anhydrous ether contained in a flask that was connected with an inverted condenser and with a hydrogen generator. The ether was boiled for a short time in order to saturate the solution, the air in the apparatus replaced with dry hydrogen, and 5 grams of magnesium and a crystal of iodine added through the condenser. The reaction began at once and proceeded quietly without further heating. When all of the halogen compound had disappeared the liquid was cooled and cautiously treated with enough concentrated hydrochloric acid to dissolve the excess of magnesium. The ethereal layer was washed, dried over fused sodium sulphate, and the ether allowed to evaporate. It deposited 6 grams of solid and a small quantity of oil. The solid was easily purified by crystallization from acetone.

Analysis:

0.1277 gram substance gave 0.4370 gram CO_2 and 0.0678 gram H_2O.

	Calculated for $C_{27}H_{20}$.	Found.
C	94.2	93.9
H	5.8	5.8

Triphenylindene separates from ether or acetone in large colorless prisms melting at 135°. It is readily soluble in chloroform and ether, moderately in acetone and alcohol, sparingly in ligroin. It is very slightly soluble in cold sul-

phuric acid and its solution in the warm acid is colorless. The hydrocarbon does not react with bromine dissolved in chloroform or boiling carbon tetrachloride but substitution takes place when bromine vapor is passed through the substance heated to 150°–160°. The only product is the yellow bromide described above.

Triphenylindene is readily oxidized with chromic acid. At the ordinary temperature the principal product is the carbinol. Thus 5 grams of chromic acid were added to 5 grams of the hydrocarbon dissolved in 100 grams of glacial acetic acid and the mixture allowed to react for 24 hours. The solution was then diluted with much water and extracted with ether. After washing with sodium carbonate and drying with sodium sulphate the ether was allowed to evaporate. It deposited a small quantity of *o*-dibenzoylbenzene and an oil that gave 4.8 grams of ethoxytriphenylindene when boiled with alcohol and a few drops of concentrated sulphuric acid. This shows that 4.5 grams of carbinol were formed by direct oxidation of the hydrocarbon. *o*-Dibenzoylbenzene is the only product that is obtained when the oxidation is carried out in boiling acetic acid.

1,1,3-Triphenylindene,
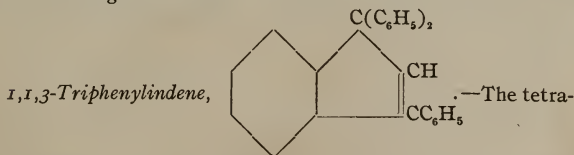
.—The tetra-

phenylallene used in the preparation of this hydrocarbon was made from tetraphenylpropyl alcohol by the excellent method of Vorländer and Siebert.[1] It was transformed into the indene derivative by passing dry gaseous hydrogen chloride into its solution in boiling glacial acetic acid. The first few bubbles of gas developed a red color in the solution. This deepened as the concentration of the acid increased, then began to fade, and in a remarkably short time—less than 5 minutes for 50 grams of substance—the solution became colorless and the transformation was complete. The solution was poured into

[1] Ber. d. chem. Ges., **39,** 1030.

ice water, the solid product removed, washed with water, and recrystallized from methyl alcohol. It melted at 135°, the same temperature at which 1,2,3-triphenylindene melts, but a mixture of the two began to melt at about 104°.

Vorländer and Siebert found that chromic acid in boiling acetic acid oxidizes the hydrocarbon and forms a product melting at 146°–148°. This is *o*-dibenzoylbenzene.

0.1309 gram substance gave 0.4078 gram CO_2 and 0.0580 gram H_2O.

	Calculated for $C_{20}H_{14}O_2$.	Found.
C	83.9	83.8
H	4.9	5.0

These results differ somewhat from those obtained by Vorländer and Siebert but a comparison of the oxidation product with some *o*-dibenzoylbenzene made from dibenzoylbenzene established the identity of the substances.

As the hydrocarbon gives *o*-dibenzoylbenzene it must be an indene derivative with phenyl groups in the 1 and 3 positions. By oxidizing at a lower temperature it is possible to get an intermediate oxidation product, the formation of which proves the presence of two phenyl groups in the 1 position.

o-Benzoyltriphenylacetic Acid, $C_6H_5COC_6H_4C(C_6H_5)_2CO_2H$.— A solution of 12 grams of chromic acid in the minimum quantity of cold water was added drop by drop to a solution of 15 grams of the hydrocarbon in glacial acetic acid. The mixture was kept cool with running water for 18 hours, then poured into ice water. The pasty precipitate was washed with water, then dissolved in ether and shaken with a saturated solution of sodium carbonate. This precipitated a sparingly soluble sodium salt that separated in needles. The salt is almost insoluble in cold water and is decomposed by boiling water. It was washed with water and recrystallized by solution in methyl alcohol and cautious addition of ether. It was thus obtained in small colorless prisms, melting with decomposition at about 130°.

Analysis:

0.3220 gram substance gave 0.0542 gram Na_2SO_4.

	Calculated for $C_{27}H_{19}O_8Na.H_2O$.	Found.
Na	5.32	5.5

In order to get the acid the sodium salt was suspended in ether and shaken with dilute hydrochloric acid. The ethereal layer was dried and the ether allowed to evaporate. The resulting solid was purified by crystallization from a mixture of ether and ligroin. It separated in small prisms that melted with decomposition at 230°.

Analysis:

0.1311 gram substance gave 0.3971 gram CO_2 and 0.0614 gram H_2O.

	Calculated for $C_{27}H_{20}O_8$.	Found.
C	82.7	82.6
H	5.1	5.2

The formation of *o*-benzoyltriphenylacetic acid and *o*-dibenzoylbenzene, by oxidation, shows that the formula proposed by Vorländer and Siebert is correct and that tetraphenylallene very readily undergoes rearrangement to 1,1,3-triphenylindene.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

CLVIII. — RESEARCHES ON PYRIMIDINES: SYNTHESIS OF CYTOSINE-5-CARBOXAMIDE.

[THIRTY-SIXTH PAPER.[1]]

BY HENRY L. WHEELER AND CARL O. JOHNS.

In our previous papers on the synthesis of the 5-carboxyl derivatives of uracil[2] and cytosine[3] we have shown that Claisen's ethoxymethylenemalonic ester,[4] $C_2H_5OCH = C(CO_2C_2H_5)_2$,

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[1] A complete list of our previous papers on pyrimidines up to the end of the year 1907 is given at the end of this article.
[2] THIS JOURNAL, **37**, 392 (1907).
[3] *Ibid.*, **38**, 594 (1907).
[4] Ann. Chem. (Liebig), **297**, 75 (1897).

condenses in alkaline solution with 2-ethylpseudothiourea, $H_2N—C(SC_2H_5) = NH$, giving 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine (Formula I., on page 237). The condensation is especially smooth. We have succeeded in greatly increasing the yield of pyrimidine over the amount obtained in our first experiments and this condensation now offers an excellent starting point for further syntheses. We have also previously shown that 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine is easily saponified by alkali and the yield of 2-ethylmercapto-6-oxypyrimidine-5-carboxylic acid, II., is very good.

We now find that with proper precautions this mercapto acid can be practically quantitatively converted into the acid chloride of 2-ethylmercapto-6-chlorpyrimidine-5-carboxylic acid, III. This acid chloride is a very reactive substance and, as might be expected, the chlorine attached to the CO group is more reactive than that in the 6 position.

When the dichloride is treated with cold aqueous ammonia one chlorine atom is replaced by the amino group and 2-ethylmercapto-6-chlorpyrimidine-5-carboxamide, IV., results. This is proved by the fact that on treating the chloramide with sodium ethylate an ethoxy derivative, V., is obtained which is isomeric and not identical with 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine, X.

When the dichlorpyrimidine is warmed with concentrated aqueous ammonia on the steam bath, both chlorine atoms are removed and it is quantitatively converted into 2-ethylmercapto-6-aminopyrimidine-5-carboxamide, VI.

We have found that this acid amide combines with bromine with the evolution of heat and that the product has the properties and composition of a dibrom addition product, VII. When it was treated with alkali it regenerated unaltered 2-ethylmercapto-6-aminopyrimidine-5-carboxamide.

When it was heated under certain conditions, its loss in weight and percentage of nitrogen corresponded with that required for the formation of a monobromamide. If a monobromamide was formed here it might be expected that, in common with such substances, on treatment with alkali the bromamide group, RCONHBr, would undergo a rearrange-

ment into the carbonamide form, RNCO. In this case the reactive grouping would probably unite with the adjacent amino group in the 6 position, forming a five membered ring, with the result that an 8-oxypurine would be obtained.

When the product or mixture obtained by heating the dibrom addition product was treated with aqueous alkali, cytosine-5-carboxylic acid, VIII., sometimes 2-ethylmercapto-6-aminopyrimidine-5-carboxamide, VI., and a product free from sulphur was obtained. This latter substance and its salts gave results on analysis which closely agreed with the calculated for 2,8-dioxypurine, XI., the only one of the dioxypurines that has not been described. The empirical formula of 2,8-dioxypurine, $C_5H_4O_2N_4$, differs from cytosine-5-carboxamide, IX., $C_5H_6O_2N_4$, by only two hydrogen atoms. The percentage composition of these substances is therefore so closely similar that the analysis did not decide which one of the two we were dealing with. In our previous work we had reason to believe that we had obtained cytosine-5-carboxamide, IX. With the object of preparing this substance, the behavior of the ethyl ester of cytosine-5-carboxylic acid, or 5-carbethoxy-cytosine, XII., with aqueous ammonia was examined at that time and it was found that this ether showed an exceptional inertness. On heating at 140° to 150° for two hours, about 25 per cent remained unaltered. On concentrating the mother liquor more soluble material crystallizing in needles was obtained. The analytical results in this case and the method of preparation were then taken to indicate that the expected cytosine-5-carboxamide had been obtained. Owing to the poor yield, nothing further was done with this substance.

This material was not identical with that obtained in the present work. The facts then seemed to show that the material obtained from the brom addition product, VII., was 2,8-dioxypurine. The question was finally settled in the negative, as follows: The material obtained by heating the dibromamide and then treating with alkali was carefully freed from 2-ethylmercapto-6-aminopyrimidine-5-carboxamide and cytosine-5-carboxylic acid. It was then boiled with strong hydrochloric acid and found to completely decompose into cytosine-5-carboxylic acid.

This shows that no Hofmann rearrangement had taken place and that the present substance is the true cytosine-5-carboxamide.

The inertness of 5-carbethoxycytosine, and also of 2,6-diamino-5-carbethoxypyrimidine,[1] on heating with ammonia, is comparable with that of the dialkylmalonic esters.[2] The ammonium salts of these acids break down with the evolution of carbon dioxide, and since 5-carbethoxycytosine is a substituted malonic acid derivative this offers an explanation of our previous results. The material formerly viewed as cytosine-5-carboxamide was probably impure or partly hydrous cytosine.

It is probable that no monobromamide was formed on heating the dibrom addition product and that the dibrom addition product has the bromine atoms attached to the double bond between the 4 and 5 positions. Similar additions of bromine to the double bond have been observed in other cases in this laboratory, *e. g.*, thymine and 4,5-dimethyluracil. The compounds in general have little stability. An unusually stable dibrom addition product of this sort, prepared from 2-phenylhydrazine-4-methyl-6-oxypyrimidine, has been described by Pellizzari and Roncagliolo.[3]

When 2-ethylmercapto-6-aminopyrimidine-5-carboxamide, VI., was boiled with hydrochloric acid it was converted into cytosine-5-carboxylic acid. When given a less energetic treatment with acid, in addition to unaltered material, some cytosine-5-carboxamide along with cytosine-5-carboxylic acid was obtained. This amide was identical with that obtained from the brom product.

The question whether or not the Hofmann rearrangement can be applied in the pyrimidine series still remains to be investigated. A 2-oxygen amide such as cytosine-5-carboxamide, being soluble in alkali and free from sulphur, would be a more promising substance than the mercaptoamide to decide this question. The work will be undertaken as soon

[1] This Journal, **38**, 598 (1907).
[2] Fischer and Dilthey: Ber. d. chem. Ges., **35**, 844.
[3] Gaz. chim. ital., **31**, I, 513.

as a more convenient method of preparing this amide, in quantities sufficient for synthetical purposes, is obtained.

It appears from the above results that the unsaturated condition of the molecule, or the double bond in the 4,5 position, interferes with the Hofmann rearrangement, at least in the case of 2-ethylmercapto-6-aminopyrimidine-5-carboxamide.

$$
\begin{array}{ccc}
\text{HN — CO} & \text{HN — CO} & \text{N = CCl} \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CCO}_2\text{C}_2\text{H}_5 \rightarrow & \text{C}_2\text{H}_5\text{SC} \quad \text{CCOOH} \rightarrow & \text{C}_2\text{H}_5\text{SC} \quad \text{CCOCl} \\
\text{N — CH} & \text{N — CH} & \text{N — CH} \\
\text{I.} & \text{II.} \quad \swarrow & \text{III.}
\end{array}
$$

$$
\begin{array}{ccc}
\text{N = C — NH}_2 & \text{N = CCl} & \text{N = COC}_2\text{H}_5 \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CCONH}_2 \leftarrow & \text{C}_2\text{H}_5\text{SC} \quad \text{CCONH}_2 \rightarrow & \text{C}_2\text{H}_5\text{SC} \quad \text{CCONH}_2 \\
\text{N — CH} & \text{N — CH} & \text{N — CH} \\
\text{VI.} & \text{IV.} & \text{V.}
\end{array}
$$

$$
\updownarrow \qquad \searrow
$$

$$
\begin{array}{ccc}
\text{N = C — NH}_2 & \text{N = C — NH}_2 & \text{N = C — NH}_2 \\
\text{C}_2\text{H}_5\text{SC} \quad \text{C} \diagdown^{\text{CONH}_2}_{\text{Br}} \rightarrow & \text{OC} \quad \text{CCONH}_2 & \text{C}_2\text{H}_5\text{SC} \quad \text{CCOOC}_2\text{H}_5 \\
\text{N — CHBr} & \text{HN — CH} & \text{N — CH} \\
\text{VII.} & \text{IX.} & \text{X.}
\end{array}
$$

$$
\downarrow \qquad \swarrow
$$

$$
\begin{array}{ccc}
\text{N = C — NH}_2 & \text{N = C — NH} \diagdown & \text{N = C — NH}_2 \\
\text{OC} \quad \text{CCOOH} & \text{OC} \quad \text{C — NH} \diagup^{\text{CO}} & \text{OC} \quad \text{CCOOC}_2\text{H}_5 \\
\text{HN — CH} & \text{HN — CH} & \text{HN — CH} \\
\text{VIII.} & \text{XI.} & \text{XII.}
\end{array}
$$
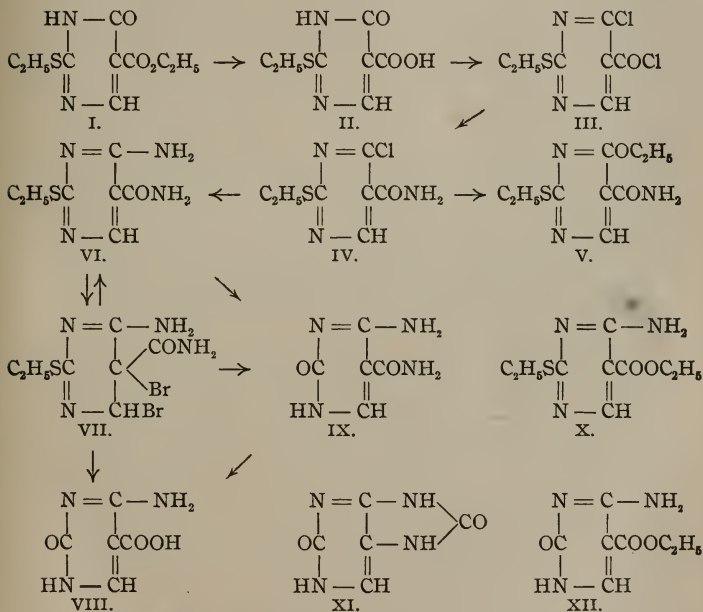
EXPERIMENTAL PART.

Ethoxymethylenemalonic Ester, $C_2H_5OCH = C(CO_2C_2H_5)_2$. — Since this ester has proved to be of special importance for pyrimidine syntheses a detailed account is given of our methods of preparing and employing the substance.

The ester was prepared essentially according to Claisen's directions.[1] We have found that the mixture of malonic ester (100 grams), orthoformic ester (93 grams), acetic anhydride (128 grams), and zinc chloride (7 grams) reacts immediately on gently warming and enough heat is evolved to boil the solution. The mixture was kept boiling for an hour, then all that distilled up to 110° at ordinary pressure (the bulb of the thermometer being *in the solution*) was removed. The distillate usually weighed about 52 grams and represented the ethyl acetate formed in the reaction. A little anhydride was usually carried over.

It was found that it is unnecessary to boil the above mixture for 11–12 hours, as stated by Claisen. In fact, heating the flask attached to a return condenser in an oil bath at 120°–130°, or so that the mixture boiled gently, for two more hours was sufficient. There were then obtained 14–15 grams of impure ethyl acetate or about 67 grams in all, which is 60 per cent of the calculated. The calculated yield of ethyl acetate is 110 grams. Boiling for a longer time gave very little more ethyl acetate. A portion of the ethyl acetate, however, probably remains behind in the mixture.

The mixture was then distilled at 15–20 mm. pressure and in almost every case 60–62 grams of ethoxymethylenemalonic ester were obtained. Sixty-two grams of ethoxymethylenemalonic ester is only 45.9 per cent of the calculated. However, this yield is in perfect agreement with Claisen's statement that 500 grams of malonic ester, in five portions, gave 307 grams of distilled ethoxymethylenemalonic ester. The amount of ethyl acetate obtained indicated that at least 81 grams of ethoxymethylenemalonic ester was formed from 100 grams of malonic ester.

We have now found that it is not necessary or even advisable, on account of loss, to prepare pure distilled ethoxymethylenemalonic ester for the present condensation. In fact, a much better yield of condensation product is obtained if the oil is not distilled.

[1] Ann. Chem. (Liebig), **297**, 75 (1897).

Preparation of the Potassium Salt of 2-Ethylmercapto-5-carb-

$$\begin{array}{ccc} HN & — & CO \\ | & & | \\ C_2H_5SC & & CCO_2C_2H_5. \\ \| & & \| \\ N & — & CH \end{array}$$
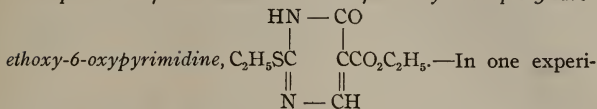
ethoxy-6-oxypyrimidine, C_2H_5SC $CCO_2C_2H_5$.—In one experi-

ment, after heating the above mixture at ordinary pressure for three hours, distilling the ethyl acetate as stated, and filtering from zinc chloride, everything was then removed that distilled below 117° at about 20 mm. pressure. The residue in this case weighed 105 grams. This was added to 100 grams of the addition product of ethyl bromide and thiourea dissolved in 100 cc. of water. To this cold solution 60 grams of potassium hydroxide in 120 cc. of water were slowly added and the mixture was not allowed to warm. The solution soon became semisolid from the separation of the potassium salt. It was found that more separated on standing. The mixture was allowed to stand for two days at ordinary temperature. The salt which separated then, on filtering and drying, weighed 113 grams, or nearly twice as much crude salt as was obtained from 100 grams malonic ester in our previous work.

In another experiment everything was removed that distilled below 120° at 25 mm. pressure. The remaining oil weighed 100 grams. When this was condensed with 2-ethylpseudothiourea as above, the weight of the potassium salt, after washing with a little alcohol, was 91 grams.

The above yields, of course, do not represent the weights of pure substances, they merely serve to give a general idea. We conclude, however, that the above process yields almost 75 per cent of the calculated of ethoxymethylenemalonic ester; 105 grams is 77.7 per cent of the calculated.

Preparation of 2-Ethylmercapto-6-oxypyrimidine-5-carboxylic

$$\begin{array}{ccc} HN & — & CO \\ | & & | \\ C_2H_5SC & & CCOOH. \\ \| & & \| \\ N & — & CH \end{array}$$
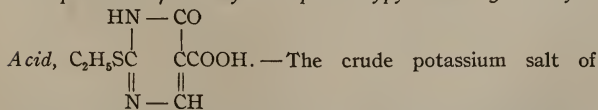
Acid, C_2H_5SC $CCOOH$.— The crude potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine was saponified

by warming with potassium hydroxide. For about 27–30 grams of this salt 15 grams of potassium hydroxide were used. If a smaller proportion of alkali was used the saponification was liable to be less smooth.

The potassium salt was dissolved in alcohol, the alkali in water added, and the solution evaporated to dryness on the steam bath. The residue was taken up in water and evaporated again, when the saponification was usually found to be complete. The acid was then precipitated from the filtered aqueous solution of this residue by means of hydrochloric acid. It separated in an almost pure condition as shown by its melting point (near 167°). Care must be taken not to add too much hydrochloric acid since the mercapto acid is soluble in a certain excess. On the other hand, if the solution is not made distinctly acid, the potassium salt of 2-ethylmercapto-6-oxypyrimidine-5-carboxylic acid is obtained. This melts with effervescence above 250°. If the precipitate melts near 131° the saponification is not complete.

Twenty-seven grams of the washed potassium salt gave 17 grams of 2-ethylmercapto-6-oxypyrimidine-5-carboxylic acid. The same quantity of salt in another experiment gave 18 grams of acid. This is 88.6 per cent of the calculated.

The Acid Chloride of 2-Ethylmercapto-6-chlorpyrimidine-5-carboxylic Acid,

$$C_2H_5SC\begin{matrix} N = CCl \\ | \quad\quad | \\ \\ || \quad\quad || \\ N — CH \end{matrix}CCOCl.$$

—The best yield of this compound was obtained when perfectly dry 2-ethylmercapto-oxypyrimidine-5-carboxylic acid and phosphorus oxychloride were mixed in the proportion of 5 cc. of the chloride to 1 gram of the acid and then heated, with a return condenser, in an oil bath. The temperature of the bath was kept at 130°–150° or so that the solution boiled quietly and until hydrogen chloride was no longer evolved. This required from 2 to 3 hours, although solution took place soon after heating. Most of the phosphorus oxychloride was then removed under reduced pressure at 100° and the residue, a thick oil, was poured upon

cracked ice. It then changed to a granular solid. The yield of crude chloride was 85 per cent of the calculated. To prepare the amide of 2-ethylmercapto-6-aminopyrimidine-5-carboxylic acid, instead of pouring on ice, it is poured directly into concentrated ammonia (see below). The yield of crude amide is then almost quantitative. In another experiment 18 grams of the acid and 45 cc. of phosphorus oxychloride were boiled on a sand bath. Under these conditions the material was completely decomposed. The yield of this chloride may vary decidedly under slight changes of conditions.

This acid chloride was very soluble in cold benzene, ether, and ligroin. It was purified for analysis by dissolving in ligroin and evaporating at the temperature of the room. Radiating clusters of colorless prisms were formed, which melted to a clear oil at 38°–40°. Analysis:

	Calculated for $C_7H_6ON_2Cl_2S$.	Found.
N	11.81	11.76

The Amide of 2-Ethylmercapto-6-chlorpyrimidine-5-carboxylic

$$\begin{array}{cc} N = CCl \\ | \quad | \\ Acid, \ C_2H_5SC \quad CCONH_2.\text{—This is the first product obtained} \\ || \quad || \\ N — CH \end{array}$$
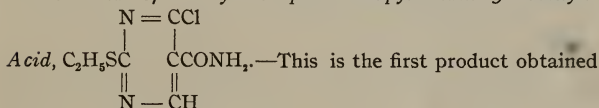
by the action of aqueous ammonia on the above acid chloride. When the acid chloride was added to cold concentrated aqueous ammonia, an immediate reaction took place with the liberation of heat and a white powder was formed. This was washed with water to remove ammonium chloride. When dried it was found to be moderately soluble in hot alcohol, benzene, and toluene, and difficultly soluble in boiling ether. It crystallized from benzene in long, hairlike crystals which formed a fibrous mat. It then melted sharply to a colorless oil at 134° and the yield was almost quantitative. Analysis:

	Calculated for $C_7H_8ON_3ClS$.	Found. I.	Found. II.
N	19.31	19.36	19.24

When this chloramido compound was first obtained it became a question which chlorine atom had been replaced in the above

acid chloride. In order to decide this point, two grams of the chloramido compound were dissolved in absolute alcohol and added to a solution of 0.25 gram of sodium, also in alcohol. An immediate precipitate resulted and heat was liberated. On cooling, a mass of well defined prisms separated. The sodium chloride was removed by washing with water. The residue was then found to be insoluble in hot water but it crystallized from alcohol, in which it was moderately soluble. The substance melted at 134°, the same temperature as the chloramido compound. However, it was free from chlorine and when mixed with the chloramido compound the melting point of the mixture was lowered about 30°. The yield and nitrogen determinations agreed with the calculated for an ethoxy derivative.

	Calculated for $C_9H_{13}O_2N_3S$.	Found. I.	Found. II.
N	18.50	18.54	18.45

This ethoxy derivative should have the structure represented by one of the following formulas:

$$
\begin{array}{cc}
\text{N} = \text{C} - \text{NH}_2 & \text{N} = \text{COC}_2\text{H}_5 \\
\mid \qquad \mid & \mid \qquad \mid \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CCO.OC}_2\text{H}_5 & \text{C}_2\text{H}_5\text{SC} \quad \text{CCO.NH}_2. \\
\parallel \quad \parallel & \parallel \quad \parallel \\
\text{N} - \text{CH} & \text{N} - \text{CH} \\
\text{I.} & \text{II.}
\end{array}
$$
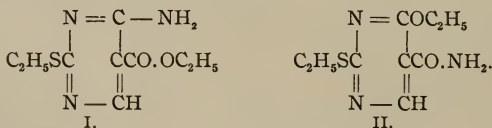
The first of these two compounds has already been described by us in our twenty-sixth paper, p. 597. It melts at 102°. To the ethoxy compound now obtained, melting at 134°, is therefore assigned the structure represented by formula II. It follows that the chloride from which it was prepared has the chlorine atom in the 6 position and is the amide of 2-ethylmercapto-6-chlorpyrimidine-5-carboxylic acid.

The Amide of 2-Ethylmercapto-6-aminopyrimidine-5-carboxylic

$$
\begin{array}{c}
\text{N} = \text{C} - \text{NH}_2 \\
\mid \qquad \mid \\
\textit{Acid,} \quad \text{C}_2\text{H}_5\text{SC} \quad \text{CCONH}_2. \text{---If the acid chloride of 2-ethyl-} \\
\parallel \quad \parallel \\
\text{N} - \text{CH}
\end{array}
$$

mercapto-6-chlorpyrimidine-5-carboxylic acid is warmed with

concentrated ammonia both chlorine atoms are replaced by the amino group and the amide of 2-ethylmercapto-6-amino-pyrimidine-5-carboxylic acid is formed. We have prepared this compound by slowly adding the acid chloride (it reacts vigorously) to a considerable excess of aqueous ammonia in an evaporating dish and then warming on the steam bath. Not very much of the aminoamide thus formed dissolves in the hot ammonia nor is it soluble to any great extent in boiling water. It should be warmed until the insoluble material melts above 200°. When purified by crystallizing from alcohol, in which it is moderately soluble, it separates in rectangular crystals, little stout prisms which separate slowly and melt to an oil at 218°–219°. It is soluble in glacial acetic acid but insoluble in alkali. The yield of crude product melting at 214° is almost quantitative. Thirteen grams of mercapto acid gave 12 grams of this amide. Analysis:

	Calculated for $C_7H_{10}ON_4S$.	Found.	
		I.	II.
N	28.28	27.99	27.91

Action of Hydrochloric Acid.—When this amide is digested on the steam bath with concentrated hydrochloric acid ethyl mercaptan is evolved and the amido group attached to the carboxyl radical in position 5 is removed. If the resulting solution is allowed to cool slowly the *hydrochloride of cytosine-5-carboxylic acid* separates in the form of large prisms which contain one molecule of water and melt sharply at 276° to a brown oil and with some effervescence. This salt was identified by its properties previously described and by the following analyses:

	Calculated for $C_5H_5O_3N_3.HCl.H_2O$.	Found.
H_2O	8.59	8.75

The water determination was made by heating the substance at 120°–130°. A nitrogen determination then gave the following results:

	Calculated for $C_5H_5O_3N_3.HCl$.	Found.
N	21.92	22.21

Prolonged digestion of the aminoamide with dilute hydrochloric acid or potassium hydroxide also removed the amido group from the 5 position. For a description of the less energetic action of hydrochloric acid on this amide see under cytosine-5-carboxamide. It did not dissolve in a solution of potassium hypobromite (16 grams of bromine in 280 cc. of 10 per cent alkali).

The Action of Dry Bromine: The Dibrom Addition Product of 2-Ethylmercapto-6-amino-5-carboxamide,

$$
\begin{array}{c}
\text{N} = \text{C} - \text{NH}_2 \\
|\qquad| \\
\text{C}_2\text{H}_5\text{SC}\quad\text{CCONH}_2\text{Br}_2. \\
||\qquad|| \\
\text{N} - \text{CH}
\end{array}
$$
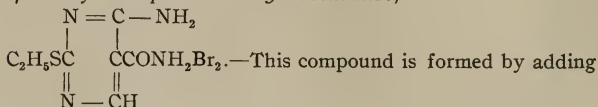
—This compound is formed by adding the amide directly to liquid bromine. They unite with evolution of considerable heat. Eight grams of finely powdered and carefully dried amide were added in small portions, best through a sieve to prevent the formation of lumps, to about 15 cc. of dry bromine. The amide then dissolved at once in the bromine. When all of the amide had been added the excess of bromine was allowed to evaporate at the temperature of the room. This treatment left a yellow, crystalline crust that was powdered in a mortar in order to liberate the inclosed bromine. The yield at this point was quantitative if care was taken to exclude moisture; otherwise some decomposition took place. Analyses of the air-dried material gave the following results:

	Calculated for $C_7H_{10}ON_4Br_2S$.	I.	II.
		Found.	
N	15.64	15.50	15.91

When the dibrom addition product was warmed with water unaltered amide was obtained.

Action of Alkali.—The unaltered amide was also obtained when this material was treated with alkali. One gram of the addition product was added to 10 cc. of water containing 1 gram of potassium hydroxide. Only a small portion dissolved even after heating on the steam bath. On filtering and acidifying the filtrate with acetic acid a very small amount of material not soluble in ammonia was precipitated. This had all the

properties of cytosine-5-carboxamide. Its hydrochloric acid solution gave a precipitate with nitric acid.

Behavior on Heating.—When the dibrom addition product was heated at 120°–135° a point was finally reached where the evolution of hydrogen bromide seemed to stop or proceed more slowly. The brownish white material then agreed in weight with the loss of about one molecular proportion of hydrogen bromide. There was a loss from 13.5 grams of the addition product of 3.3 grams while the calculated loss is 3.1 grams. Nitrogen determinations gave the following results:

	Calculated for $C_7H_9ON_4BrS$.	I.	II.
N	20.21	20.47	20.76

This product had an odor similar to that of the sulphur chlorides. It dissolved only partially in hot water, alcohol, ethyl acetate, or amyl acetate, and it behaved like a mixture of more or less decomposed material. It dissolved partially in a solution of sulphur dioxide, and ammonia then precipitated unaltered mercaptoaminoamide. This might result from the hydrobromic acid salt of the amide possibly contained in the mixture, or from unaltered dibrom addition product. A solvent suitable to isolate a monobromamide, if formed here, was not found, and the results obtained on treating the material with alkali would suggest that in spite of the analyses such a compound was not formed. Sometimes the product would dissolve completely in alkali. When dark in color it usually left undissolved amorphous, dark colored decomposition products mixed at times with unaltered mercaptoaminoamide.

$$N = C — NH_2$$

Cytosine-5-carboxamide, OC⠀⠀CCONH₂. — Ten grams of

$$HN — CH$$
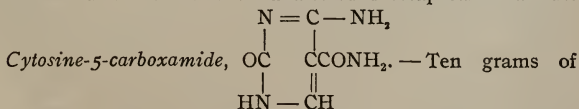
the brom product obtained by heating the above dibrom addition product of the amide of 2-ethylmercapto-6-amino-pyrimidine-5-carboxylic acid were dissolved in 50 cc. of water containing 10 grams of potassium hydroxide. In this particular experiment complete solution resulted. On acidifying with

acetic acid mercaptan was evolved and a granular precipitate was obtained. This was filtered and dissolved in hot water to which a little hydrochloric acid was added. The hot solution was then made strongly alkaline with ammonia which reprecipitated the base. This treatment removed any cytosine-5-carboxylic acid that was present, the acid being soluble in ammonia. The best yield of aminoamide obtained at this point was about 75 per cent of the theory. It varied considerably. For analysis the aminoamide was purified by recrystallizing from dilute hydrochloric acid. The hydrochloride was then dissolved in water, with the aid of a little hydrochloric acid, and the base reprecipitated with ammonia, washed thoroughly with water and alcohol, and finally dried over calcium chloride. It did not lose water when heated at 120°–130° (Analyses I. II. and III.).

When we first obtained this material attempts were made to determine nitrogen by Kjeldahl's method and it was found that neither the free base nor any of its salts that we tried gave results agreeing with the calculated. The figures invariably came several per cent too low. It appears probable that the failure to obtain correct results by Kjeldahl's method was due to the fact that the weakly basic properties of the compound permitted the escape of material on heating the sulphuric acid solution. This might have escaped unnoticed if we had no theory to check the results.

I. 0.0763 gram of substance gave 24.6 cc. of nitrogen at 22° and 770 mm. pressure.

II. 0.2462 gram of substance gave 0.0877 gram of H_2O and 0.3575 gram of CO_2.

III. 0.1440 gram of substance gave 0.0526 gram of H_2O and 0.2093 gram of CO_2.

	Calculated for $C_5H_6O_2N_4$.		Found.		
		I.	II.	III.	IV.
C	38.96	39.60	39.58	. . . . .	. . . . .
H	3.89	4.00	3.90	. . . . .	. . . . .
N	36.36	. . . . .	. . . . .	37.00	36.38

Cytosine-5-carboxamide was also obtained by the action of concentrated hydrochloric acid on 2-ethylmercapto-6-amino-

pyrimidine-5-carboxamide. One gram of the mercapto-aminoamide was evaporated to dryness with 15 cc. of concentrated hydrochloric acid on the steam bath. The residue was made strongly alkaline with ammonia. This extracted cytosine-5-carboxylic acid and left a mixture which was boiled with alcohol. Unaltered mercaptoaminoamide dissolved. The insoluble material was purified by dissolving in dilute hydrochloric acid and precipitating with an excess of ammonia while the solution was hot. This gave very small, microscopic, lenticular crystals that did not show signs of melting at 310°. When a drop of nitric acid was added to the hydrochloric acid solution a precipitate of the nitrate was formed. (Analysis IV.).

Cytosine-5-carboxamide is almost insoluble in water and the ordinary organic solvents. It dissolves readily in cold alkalies, but it is almost insoluble in ammonia. It does not dissolve in acetic acid. It dissolves in dilute mineral acids and yields beautiful crystalline salts which are dissociated by water. The aminoamide is a weak base. Its solubility in alkali is in accordance with the presence of —NH—CO— groups. The free aminoamide prepared from the brom derivative, when obtained by precipitating from alkaline solution by acetic acid or from the hydrochloric acid solution with ammonia, usually appears to be an amorphous powder. Before purifying it has a more or less brownish color. Its method of separation along the lines of stirring indicates a crystallization but the crystals are too minute to be determined under the microscope.

Action of Concentrated Hydrochloric Acid on Cytosine-5-carboxamide: *Cytosine-5-carboxylic Acid.*—The amide obtained from the bromamide (0.6 gram) was boiled with 50 cc. of concentrated hydrochloric acid for about five minutes and the resulting solution evaporated to dryness on the steam bath. The residue dissolved completely in ammonia. On acidifying with acetic acid a precipitate of cytosine-5-carboxylic acid was obtained. This decomposed at 256°. Analysis:

	Calculated for $C_5H_5O_8N_3$.	Found.
N	27.09	27.53

This acid was described in a previous paper. It should be added that, like the amide, it is almost insoluble in water and alcohol. It was obtained in an amorphous condition. When precipitated from its solution in ammonia by acetic acid it separates as a gelatinous precipitate which is difficult to filter. It is better to obtain the acid by evaporating the ammonia solution. It then separates as a finely divided powder which is readily filtered. It is also readily identified by its decomposing point, 256°, and its crystalline hydrochloride which contains 1 molecule of water of crystallization.

Cytosine-5-carboxamide Hydrochloride, $C_5H_6O_2N_4.HCl$.—The base dissolved in moderate quantities in hot dilute hydrochloric acid. On cooling, the hydrochloride separated almost completely in clusters of colorless, stout, pointed prisms which did not have a definite melting point. They did not lose weight on heating at 110°, when dried over calcium chloride. When heated at 140°–150° they lost their lustre, hydrochloric acid being slowly given off. The salt was dried at 110° for analysis:

I. 0.0739 gram of substance gave 19.0 cc. of N at 22° and 768 mm.

II. 0.0791 gram of substance gave 0.0607 gram of AgCl.

	Calculated for $C_5H_6O_2N_4.HCl$.	Found. I.	II.
N	29.40	29.42	. . . . .
Cl	18.64	. . . . .	18.97

Cytosine-5-carboxamide Nitrate, $C_5H_6O_2N_4.HNO_3$.—This is the most difficultly soluble and characteristic salt. It is formed not only by dissolving the amide in hot nitric acid but also on adding nitric acid to solutions of other salts of the base.

Cytosine-5-carboxamide dissolved very slightly in hot nitric acid. On cooling, the nitrate separated in beautiful truncated octahedrons. When nitric acid was added to a solution of the base in dilute hydrochloric acid an immediate crystalline precipitate of the nitrate came down. It then formed tufts of short hairs, which did not decompose at 300°, although they sublimed slowly below that temperature. They did not lose weight on heating at 115°. Analysis:

	Calculated for $C_5H_6O_2N_4.HNO_3$.	Found.
N	32.26	32.05

Cytosine-5-carboxamide Sulphate, $(C_5H_6O_2N_4)_2H_2SO_4$.—A solution of the amide was made in hot water containing about 10 per cent sulphuric acid. The sulphate separated, on cooling, in scales with a pearly lustre. They did not melt at 300° and no loss in weight took place on heating at 110°. Analysis:

0.0653 gram of substance gave 0.0386 gram $BaSO_4$.

	Calculated for $(C_5H_6O_2N_4)_2H_2SO_4$.	Found.
S	7.88	8.11

Cytosine-5-carboxamide Picrate, $C_5H_6O_2N_4.C_6H_2(NO_2)_3OH$.— The amide was dissolved in hot water to which a few drops of hydrochloric acid had been added. On adding an aqueous solution of picric acid an immediate precipitate was formed. This crystallized from an aqueous solution of picric acid. It dissociates in water into small, yellow prisms that began to decompose at about 260°–270°. The salt was found to be anhydrous.

I. 0.0531 gram of substance gave 11.6 cc. of N at 20° and 771 mm.

II. 0.0967 gram of substance gave 21.2 cc. of N at 18° and 771 mm.

	Calculated for $C_{11}H_9O_9N_7$.	I.	II.
		Found.	
N	25.59	25.34	25.64

The papers on pyrimidines which have been published from this laboratory, under the direction of Dr. Treat B. Johnson and the writer, have appeared in two journals. Some of these papers have not been numbered and one has received an incorrect number, there being two twenty-first papers. For the sake of reference a complete list of these papers up to the end of the year 1907 is now given. The papers are arranged and numbered in the order in which they appeared. The numbers correspond with those already given in the literature, with the exception of the paper which has been incorrectly numbered. By referring to this paper as the twenty-

fourth the order then remains otherwise undisturbed. The following is a complete list up to the end of the year 1907.

1. Researches on the Cycloamidines: Pyrimidine Derivatives. H. L. Wheeler: This Journal, **20,** 481 (1898).

2. On Some Condensation Products of the Pseudothioureas: Synthesis of Uracil, Thymine, and Similar Compounds. Henry L. Wheeler and Henry F. Merriam: This Journal, **29,** 478 (1903).

3. Syntheses of Aminooxypyrimidines having the Composition of Cytosine: 2-Amino-6-oxypyrimidine and 2-Oxy-6-aminopyrimidine. Henry L. Wheeler and Treat B. Johnson: This Journal, **29,** 492 (1903).

4. On Cytosine or 2-Oxy-6-aminopyrimidine from Triticonucleic Acid. Henry L. Wheeler and Treat B. Johnson: This Journal, **29,** 505 (1903).

5. 5-Methylcytosine. Henry L. Wheeler and Treat B. Johnson: This Journal, **31,** 591 (1904).

6. Synthesis of 2-Amino-5-methyl-6-oxypyrimidine. Treat B. Johnson and Samuel H. Clapp: This Journal, **32,** 130 (1904).

7. 2-Oxy-4,6-diaminopyrimidine. Henry L. Wheeler and George S. Jamieson: This Journal, **32,** 342 (1904).

8. The Structure of Some Substitution Products. Henry L. Wheeler and H. Stanley Bristol: This Journal, **33,** 437 (1905).

9. The Action of Potassium Thiocyanate upon Some Imidechlorides. Henry L. Wheeler and H. Stanley Bristol: This Journal, **33,** 448 (1905).

10. The Action of Aqueous and Alcoholic Ammonia and Aniline on Some Halogen- and Mercaptopyrimidines. Treat B. Johnson and Carl O. Johns: This Journal, **34,** 176 (1905).

11. 2-Ethylmercapto-5-amino-6-oxypyrimidine. Treat B. Johnson: This Journal, **34,** 191 (1905).

12. 2,5-Diamino-6-oxypyrimidine. Treat B. Johnson and Carl O. Johns: This Journal, **34,** 554 (1905).

13. Some Iodopyrimidines: 5-Iodocytosine. Treat B. Johnson and Carl O. Johns: *J. Biol. Chem.,* **1,** 305 (1906).

14. On Methods of Synthesizing Isobarbituric Acid and 5-Oxycytosine. Treat B. Johnson and Elmer V. McCollum: *J. Biol. Chem.,* **1,** 437 (1906).

15. The Action of Potassium Thiocyanate upon Imidechlorides. Treat B. Johnson and Elmer V. McCollum: This Journal, **36,** 136 (1906).

16. The Formation of Purines from Ureapyrimidines. Treat B. Johnson and Elmer V. McCollum: This Journal, **36,** 149 (1906).

17. 5-Nitrocytosine and its Reduction to 2-Oxy-5,6-diaminopyrimidine. Treat B. Johnson, Carl O. Johns, and Frederick W. Heyl: This Journal, **36,** 160 (1906).

18. 5-Ethylcytosine. Treat B. Johnson and George A. Menge: *J. Biol. Chem.,* **2,** 105 (1906).

19. Synthesis of Uracil-5-carboxylic Acid. Henry L. Wheeler, Treat B. Johnson, and Carl O. Johns: This Journal, **37,** 392 (1907).

20. Some Condensation Products of a Substituted Pseudothiourea:

Synthesis of 1-Methyluracil. Treat B. Johnson and F. W. Heyl: THIS JOURNAL, **37**, 628 (1907).

21. On a Color Test for Uracil and Cytosine. Henry L. Wheeler and Treat B. Johnson: *J. Biol. Chem.*, **3**, 183 (1907).

22. On Some Salts of Cytosine, Isocytosine, 6-Aminopyrimidine, and 6-Oxypyrimidine. Henry L. Wheeler: *J. Biol. Chem.*, **3**, 285 (1907).

23. Uracil-4-carboxylic Acid. Henry L. Wheeler: THIS JOURNAL, **38**, 358 (1907).

24. The Action of Methyl Iodide on 2-Anilino-6-oxypyrimidine and the Synthesis of 2-Anilinopyrimidine. Treat B. Johnson and Frederick W. Heyl: THIS JOURNAL, **38**, 237 (1907).

25. Synthesis of Thymine-4-carboxylic Acid. Treat B. Johnson: *J. Biol. Chem.*, **3**, 299 (1907).

26. Synthesis of Cytosine-5-carboxylic Acid. Henry L. Wheeler and Carl O. Johns: THIS JOURNAL, **38**, 594 (1907).

27. Synthesis of Thymine-5'-carboxylic Acid. (Uracil-5-acetic Acid). Treat B. Johnson and Carl Frank Speh: THIS JOURNAL, **38**, 602 (1907).

28. Synthesis of 4-Methyluracil-5-acetic Acid. Treat B. Johnson and Frederick W. Heyl: THIS JOURNAL, **38**, 659 (1907).

NEW HAVEN, CONN.,
    March, 1908.

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PEROXIDASE ACCELERATORS AND THEIR POSSIBLE SIGNIFICANCE FOR BIOLOGICAL OXIDATIONS.

BY J. H. KASTLE.

As is well known, many animal and vegetable secretions and many active extracts of living tissues possess the power of inducing the oxidation of various oxidizable substances by means of hydrogen peroxide. Such oxygen carriers are held by many chemists[1] to properly belong to the group of catalysts known as enzymes or unorganized ferments and have been called peroxidases[2] to distinguish them from the oxidases proper. Among various animal secretions, raw milk has been found to give the peroxidase reaction with hydrogen peroxide and various peroxidase reagents, among which may be mentioned guaiacum, potassium iodide and starch, paraphenylenediamine, ortol, paradiethylphenylenediamine, ursol, D., guaiacol, amidol, etc. These reactions with milk have been

[1] Bach: Ber. d. chem. Ges., **37**, 1342–1348, and 2434–2440 (1904).
[2] Linossier: Compt. rend. soc. biol., **5**, 373 (1898).

turned to practical account as affording a simple means of distinguishing between raw milk and that which has been sterilized by heat.[1] Unfortunately, however, as has been pointed out by Rubner,[2] cows' milk is liable to considerable variation in peroxidase activity and hence the general usefulness of the peroxidase reaction of milk, in its original form, as a means of distinguishing between raw and cooked milk, is considerably impaired. In this connection, however, it has recently been pointed out by Kastle and Porch[3] that the peroxidase reaction of milk can be greatly intensified through the action of certain substances, especially certain of the phenols,[4] and that through the use of these substances along with the ordinary peroxidase reagents, such as guaiacum, paraphenylenediamine, and phenolphthalin, the peroxidase reaction of milk becomes a safe and valuable criterion for distinguishing between raw milk and that which has been sterilized by heat.

The results of some of our experiments with milk will serve to make this clear. The peroxidase activity of fresh specimens of cows' milk, obtained directly from the herd, and the influence thereupon of a mixture of the cresols ("Trikresol"[5]) and β-naphthol was determined, using phenolphthalin as the substance to be oxidized, in the following manner:

Tubes were prepared containing 2 cc. of a fresh specimen of cows' milk and 1 cc. of water or a 1 per cent solution of trikresol or β-naphthol, and to these was then added 1 cc. of a solution of phenolphthalin containing 0.320 milligram of the compound in the form of the neutral sodium salt, and 0.1 cc. 0.05 N hydrogen peroxide. The tubes containing these several substances were then allowed to stand for 15 minutes at ordinary temperature (about 20° C.), at the end of which time 2 cc. of 0.1 N sodium hydroxide were added to each tube. On

[1] The literature of this subject is very extensive. See: "The Chemistry of Milk," Article 10, Bulletin No. 41, Hyg. Lab., U. S. Pub. Health and Mar. Hosp. Serv., Wash., pp. 309–417.

[2] Hygienische Rundschau, **5**, 1021–1022 (1895).

[3] See: "The Peroxidase Reaction of Milk," J. Biol. Chem., **5**, 301-320 (1908).

[4] The term "phenol" is here used in its general sense.

[5] "Trikresol" is an antiseptic containing the three cresols in approximately equal proportions.

addition of the alkali the contents of the several tubes become pink to deep purplish red in color from the phenolphthalein resulting from the oxidation, and the intensity of the red color thus produced is a measure of the quantity of phenolphthalein formed and therefore a measure also of the peroxidase activity of any given specimen of milk towards phenolphthalin. In order to make these measurements as nearly quantitative as possible, the quantity of phenolphthalein produced in each observation was determined by colorimetric comparison with

Table I.—*Showing the Influence of Trikresol on the Peroxidase Activity of Cows' Milk towards Phenolphthalin.*
(*January 21, 1908.*)

Number of specimen of milk.	Phenolphthalein formed, in milligrams.		Per cent of phenolphthalin oxidized.	
	Milk + water.	Milk + trikresol.	Milk + water.	Milk + trikresol.
1	0.020	0.050	6.29	15.72
2	0.064	0.045	20.13	14.15
3	0.025	0.159	7.86	50.00
4	0.020	0.038	6.29	11.95
5	0.024	0.054	7.55	16.98
6	0.057	0.159	17.92	50.00
7	0.057	0.127	17.92	39.94
8	0.057	0.191	17.92	60.06
9	0.010	0.080	3.14	25.16
10	0.003	0.095	0.94	29.87
11	0.048	0.159	15.09	50.00
12	0.048	0.127	15.09	39.94
13	0.080	0.127	25.16	39.94
14	0.010	0.048	3.14	15.09
15	0.020	0.032	6.29	10.06
16	0.032	0.064	10.06	20.13
17	0.020	0.159	6.29	50.00
18	0.032	0.095	10.06	29.87
19	0.025	0.127	7.86	39.94
20	0.020	0.032	6.29	10.06
21	0.013	0.048	4.09	15.09
22	0.025	0.057	7.86	17.92
23	0.010	0.048	3.14	15.09
24	0.024	0.064	7.55	20.13
25	0.048	0.048	15.09	15.09
26	0.048	0.095	15.09	29.87
Average			10.16	28.16

Table II.—*Showing the Influence of β-Naphthol on the Peroxidase Activity of Cows' Milk towards Phenolphthalin.*
(*January 22, 1908.*)

Number of specimen of milk.	Phenolphthalein formed, in milligrams.		Per cent of phenolphthalin oxidized.	
	Milk + water.	Milk + β-naphthol.	Milk + water.	Milk + β-naphthol.
I	0.006	0.254	1.89	79.87
2	0.064	0.223	20.13	70.13
3	0.032	0.318	10.06	100.00
4	0.020	0.223	6.29	70.13
5	0.016	0.191	5.03	60.06
6	0.095	0.318	29.87	100.00
7	0.095	0.318	29.87	100.00
8	0.095	0.318	29.87	100.00
9	0.010	0.095	3.14	29.87
10	0.020	0.191	6.29	60.06
11	0.016	0.254	5.03	79.87
12	0.095	0.254	29.87	79.87
13	0.095	0.223	29.87	70.13
14	Trace	0.318	. . . . .	100.00
15	0.025	0.318	7.86	100.00
16	Trace	0.318	. . . . .	100.00
17	"	0.191	. . . . .	60.06
18	"	0.318	. . . . .	100.00
19	"	0.254	. . . . .	79.87
20	0.010	0.159	3.14	50.00
21	0.013	0.223	4.09	70.13
22	0.013	0.223	4.09	70.13
23	0.000	0.025	0.00	7.86
24	Trace	0.159	. . . . .	50.00
25	0.006	0.318	1.89	100.00
26	0.000	0.223	0.00	70.13
27	0.032	0.254	10.06	79.87
	Average..............		8.83	71.74

a series of standards containing known amounts of phenolphthalein, milk, alkali, and sufficient quantities of water to make the dilution the same in all cases, *viz.*, 6.1 cc. On account of the great turbidity of solutions containing milk, it is evident that such color comparisons are only approximate. It has been my experience, however, that more exact color comparisons can be made by this method than one would ordinarily suppose to be possible, and that, all things con-

sidered, the results of the observations recorded in the tables closely approximate the actual quantities of phenolphthalein formed. In Table I. are given the results of our observations on the oxidation of phenolphthalin by milk and hydrogen peroxide, with and without trikresol; and in Table II., the results obtained with and without β-naphthol.

It is evident from these results that the oxidation of phenolphthalin by the peroxidase of cows' milk and hydrogen peroxide is greatly accelerated by small amounts of a mixture of the three cresols and by β-naphthol. The degree of acceleration brought about by trikresol and β-naphthol, respectively, varies greatly, depending on the individual nature of the milk and on factors which at present are not clearly understood. With some specimens of fresh cows' milk, over thirty times as much phenolphthalin is oxidized in the presence of trikresol as is oxidized by the milk and hydrogen peroxide alone; and on an average, three times as much. Similarly, the peroxidase activity of certain specimens of milk is increased a hundredfold, at least, by small amounts of β-naphthol; and on an average, eight times as much phenolphthalin is oxidized when β-naphthol is present as is oxidized by the milk and hydrogen peroxide alone; and towards guaiacum and paraphenylenediamine, the peroxidase activity of fresh specimens of cows' milk is also greatly intensified by small amounts of phenol, the cresols, β-naphthol, etc. As a matter of fact, the delicacy of the peroxidase reaction of milk is so greatly intensified by means of such peroxidase accelerators that by means of the test in its present form it has been found possible to readily distinguish between raw and heated milks, using single drops of milk and of the several reagents required, and through the use of these accelerators the peroxidase reaction of milk has been brought within the range of the most delicate chemical reactions (by the wet method). The question, therefore, naturally suggests itself: Is the accelerating action of such substances as phenol, the cresols, and β-naphthol, confined to the peroxidase of milk or is the peroxidase activity of other secretions and tissues intensified by these and similar substances? Without entering into all of the details of the experiments, it may be said in general that the activity of the

peroxidases from whatever source thus far obtained has been found to be greatly increased by phenol, the cresols, and β-naphthol, so that the effect of such substances on the progress of peroxidase oxidations seems to be characteristic of the peroxidases as a class and by no means confined to the peroxidase of milk. It should be observed in this connection, however, that the amounts of these several substances required to show the greatest acceleration of the oxidation in any particular case depends, to some extent at least, on the nature and activity of the particular peroxidase under investigation. For example, with the powerful peroxidase of the root of the horse-radish the best results have been obtained by working with very small amounts, both of the peroxidase and the accelerator. Indeed, it has been found that, as a rule, the more active the peroxidase the smaller the quantity of accelerator required to increase the oxidation above the normal. In order to determine the effect of various substances on the activity of the peroxidase of horse-radish root, tubes were prepared containing the following substances: 1 cc. of water, 0.05 cc. of water or of a 1 per cent solution of the substance to be tested, 0.05 cc. of an active aqueous extract of the fresh root of the horse-radish, 1 cc. phenolphthalin containing 0.320 milligram of the compound in the form of the neutral sodium salt, and 0.1 cc. 0.05 N hydrogen peroxide. In the control experiments, the tubes contained precisely the same amounts of all these substances, the only difference being that in all of the control experiments the aqueous extract of horse-radish used had been boiled for a few moments immediately before the experiments were carried out. The tubes, including the controls, were then allowed to stand at room temperature (17° to 19° C.) for 15 minutes, at the end of which time, 1 cc. of 0.1 N sodium hydroxide was added to each tube, the color was then noted, and the amount of phenolphthalein formed was determined by color comparisons with a standard containing 0.0318 milligram phenolphthalein and 1 cc. 0.1 N sodium hydroxide, at a total dilution of 3.2 cc. The results obtained with the active peroxidase of horse-radish, together with those of the control experiments, are given in Table III.

Table III.—*Showing the Influence of Various Substances on the Peroxidase Activity of an Aqueous Extract of Horse-Radish Root.*

(a) Color produced on addition of 1 cc. 0.1 N sodium hydroxide.
(b) Colorimeter readings obtained on comparison with standard phenolphthalein containing 0.0318 milligram phenolphthalein + 1 cc. 0.1 N sodium hydroxide at a total dilution of 3.2 cc., set at one division on the colorimeter scale.
(c) Quantity of phenolphthalein formed in the oxidation, in milligrams.
(d) Amounts of phenolphthalein oxidized, in milligrams.
(e) Percentage of phenolphthalein oxidized.
(f) Results of the control experiments.

Number of experiment.	Name of substance.	(a).	(b).	(c).	(d).	(e).	(f).
1	Water	Pink	5.0	0.0063	0.00634	1.98	Faint pink[1]
2	Phenol	Red	0.6	0.0530	0.05332	16.50	Trace of pink
3	Resorcin	Red	0.5	0.0636	0.06398	19.96	"
4	Tannin	Yellowish-brown	...	......	....	......	Yellowish brown
5	β-Naphthol	Red[2]	0.3	0.1060	0.10664	33.32	Faint pink
6	o-Cresol	Deep pink	1.0	0.0318	0.03200	10.00	Trace of pink
7	m-Cresol	Red	0.5	0.0636	0.06398	19.96	"
8	p-Cresol	Red	0.4	0.0795	0.07998	25.00	"
9	Eugenol	Faint pink	6.0	0.0053	0.00533	1.66	"
10	Thymol	Pink	5.0	0.0063	0.00634	1.98	"
11	Guaiacol	Pink	5.0	0.0063	0.00634	1.98	"
12	Benzoic acid	Deep pink	2.5	0.0126	0.01268	3.96	"
13	Salicylic acid	Pink	2.5	0.0126	0.01268	3.96	"
14	Triiodophenol	Pink	4.0	0.0080	0.00805	2.50	"
15	Trikresol	Red	0.5	0.0636	0.06398	19.96	"

[1] The several amounts of phenolphthalein formed in the control experiments were too small to be determined colorimetrically.

[2] The solutions containing horse-radish peroxidase and β-naphthol frequently became pink in color even before the addition of alkali.

This change of color, before the addition of alkali, is due to the fact that the phenolphthalein undergoing oxidation in these experiments is present in the solution in the form of a neutral sodium salt. On oxidation, however, it is converted into the monosodium salt of phenolphthalein which therefore should exhibit, to a certain extent at least, the characteristic color of phenolphthalein in alkali. As the color of phenolphthalein in alkali depends, within certain limits, on the concentration of the alkali, the color is greatly intensified by the addition of sodium hydroxide,

It is evident from the results given in Table III. that thymol, eugenol, tannin, and guaiacol are practically without effect on the oxidation of phenolphthalin by horse-radish peroxidase and hydrogen peroxide. Triiodophenol and benzoic and salicylic acids slightly accelerate the oxidation. It will be observed, however, that in the presence of small amounts of phenol, the three cresols, acting singly or together, resorcin, and β-naphthol, from five to fifteen times as much phenolphthalin is oxidized by horse-radish peroxidase and hydrogen peroxide as is oxidized by the peroxidase and hydrogen peroxide alone. Instances of the acceleration of peroxidase oxidations by means of substances of the phenol type might be multiplied at length, for the reason that by means of paraphenylenediamine and phenolphthalin, evidences of such acceleration have been obtained with peroxidases from every source thus far examined, including the peroxidase of the potato, carrot, and other plants, and that of saliva, certain abnormal urines, pus, etc., etc. It is unnecessary, however, in the present discussion to give the results of all these experiments in detail. For the sake of completeness, however, a few of the experiments with fresh extract of malt and saliva are here submitted.

In order to determine the effect of phenol on the peroxidase of a fresh extract of malt, the following tubes were prepared:

(1) 1 cc. phenolphthalin, 0.1 cc. 0.05 N hydrogen peroxide, and 2.05 cc. water.

(2) 1 cc. " 0.1 cc. 0.05 N hydrogen peroxide, 0.05 cc. 1 per cent phenol, and 2 cc. water.

(3) 1 cc. " 0.1 cc. 0.05 N hydrogen peroxide, 1 cc. malt, and 1.05 cc. water.

(4) 1 cc. " 0.1 cc. 0.05 N hydrogen peroxide, 1 cc. malt, 1 cc. water, and 0.05 cc. 1 per cent phenol.

(5) 1 cc. " 0.1 cc. 0.05 N hydrogen peroxide, 1 cc. malt (boiled), 1 cc. water, and 0.05 cc. 1 per cent phenol.

These tubes were allowed to stand 15 minutes at 17° C., when 1 cc. of 0.1 N sodium hydroxide was added to each tube. The results are given in Table IV.

Table IV.

(*a*) Color produced on addition of 1 cc. 0.1 N sodium hydroxide.

(*b*) Colorimeter readings obtained on comparison with standard phenolphthalein containing 0.0318 milligram phenolphthalein + 1 cc. 0.1 N sodium hydroxide at a total dilution of 4.15 cc., set at one division on the colorimeter scale.

(*c*) Quantity of phenolphthalein formed in the oxidation, in milligrams.

(*d*) Amounts of phenolphthalin oxidized, in milligrams.

(*e*) Percentage of phenolphthalin oxidized.

Number of experiment.	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
1	Trace of pink[1]	....	......	.....	.....
2	"	....	......	......	.....
3	Pink	1.00	0.0318	0.032	10.00
4	Red	0.25	0.1272	0.128	40.00
5	Faint yellowish	....	......	.....	

Using human saliva instead of fresh extract of malt, the conditions otherwise being the same as with malt, the following results were obtained.

Table V.

Number of experiment.	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
1	Trace of pink[1]	.....	....	....	....
2	"	.....	....	....	....
3	Faint pink	12.00	0.00265	0.00267	0.83
4	Pink	5.00	0.00636	0.00640	2.00
5	Colorless	.....	....	....	....

In Tables VI. and VII. are given the results of further observations on the effect of various substances on the peroxidase activity of malt and human saliva. Tubes were prepared containing 1 cc. water, 1 cc. malt, 1 cc. phenolphthalin, 0.10 cc. 0.05 N hydrogen peroxide, and 0.05 cc. of the solution to be tested or an equal volume of distilled water. These were allowed to remain at room temperature (16°–21° C.) for 65 minutes, at the end of which time 1 cc. 0.1 N sodium hydroxide was added to each tube and the resulting colors

[1] In experiments 1, 2, and 5 the quantities of phenolphthalein formed were too small to be determined colorimetrically.

compared with a standard phenolphthalein solution containing 0.0318 milligram phenolphthalein, 1 cc. of malt, 1 cc. 0.1 N sodium hydroxide, and water sufficient to bring the total volume of the standard to 4.15 cc.

Table VI.—*Showing the Influence of Various Substances on the Peroxidase Activity of Fresh Malt Extract.*

(*a*) Color produced on addition of 1 cc. 0.1 N sodium hydroxide.

(*b*) Colorimeter readings obtained on comparison with the standard set at one division on the colorimeter scale.

(*c*) Quantity of phenolphthalein formed, in milligrams.

(*d*) Amounts of phenolphthalin oxidized, in milligrams.

(*e*) Percentage of phenolphthalin oxidized.

Number of experiment.	Name of substance.	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).
1	Water	Pink	1.25	0.0254	0.0256	8.00
2	β-Naphthol	Red	0.50	0.0636	0.0640	20.00
3	Phenol	Deep red	0.40	0.0795	0.07998	25.00
4	*o*-Cresol	Deep red	0.40	0.0795	0.07998	25.00
5	*m*-Cresol	Red	0.50	0.0636	0.0640	20.00
6	*p*-Cresol	Deep red	0.40	0.0795	0.07998	25.00
7	Resorcin	Deep pink	0.70	0.0454	0.0457	14.20
8	Thymol	Pink	1.25	0.0254	0.0256	8.00
9	Benzoic acid	Pink	1.30	0.0245	0.0247	7.70
10	Salicylic acid	Pink	1.40	0.0227	0.0228	7.10
11	Tannin	Yellowish brown	....	......	......	.....

In the experiments with human saliva, tubes were prepared containing 1 cc. of mixed saliva (human) which had previously been diluted with an equal volume of water and filtered until clear, 1 cc. phenolphthalin, 0.05 cc. of water or of a one per cent solution of the substance to be tested, and 0.10 cc. of 0.05 N hydrogen peroxide. The tubes were then allowed to stand at room temperature (21.5° to 24.5° C.) for 15 minutes, when 1 cc. 0.1 N sodium hydroxide was added to each tube and the colors produced compared with a standard containing 0.0318 milligram of phenolphthalein, 1 cc. 0.1 N sodium hydroxide, 1 cc. of saliva, and water sufficient to make the total volume of the standard equal to 3.15 cc.

Table VII.—Showing the Influence of Various Substances on the Peroxidase Activity of Human Saliva.

(a) Color produced on addition of 1 cc. 0.1 N sodium hydroxide.

(b) Colorimeter readings obtained on comparison with the standard set at one division on the colorimeter scale.

(c) Quantity of phenolphthalein formed, in milligrams.

(d) Amounts of phenolphthalin oxidized, in milligrams.

(e) Percentage of phenolphthalin oxidized.

Number of experiment.	Name of substance.	(a).	(b).	(c).	(d).	(e).
1	Water	Trace of pink[1]	3.2	0.0099	0.00996	3.1
2	β-Naphthol	Light pink	1.0	0.0318	0.032	10.00
3	Phenol	Deep pink	3.0	0.0106	0.01066	3.33
4	o-Cresol	Light pink	1.6	0.0198	0.0199	6.20
5	m-Cresol	Deep pink	1.5	0.0212	0.0213	6.65
6	p-Cresol	Deep pink	...	......	......	.....
7	Resorcin	Trace of pink	...	......	......	....
8	Thymol	"	...	......	......	....
9	Benzoic acid	"	...	......	......	....
10	Salicylic acid	"	...	......	......	....
11	Tannin	Yellowish brown	...	......	......	....

It would seem, therefore, that so far as their effect on peroxidase oxidations is concerned, substances may be arranged in three classes:

(1) Those which accelerate the oxidation.

(2) Those which exert little or no influence upon it.

(3) Those which retard it.

To class (1) belong the following substances: Phenol, the cresols, β-naphthol, resorcin, vanillin,[2] etc., all of which have been found to greatly accelerate peroxidase oxidations under certain conditions. In this class of substances might also be included iodine[3] and hydrogen ions,[4] both of which, according to Bach, intensify the action of peroxidase at certain concentrations. Dupouy[5] has made the interesting observation that magnesium sulphate augments the peroxidase activity of saliva, and Gillet[6] has found that the

[1] In experiments 1, 7, 8, 9, 10, and 11, the quantity of phenolphthalein formed was too small to be determined colorimetrically.

[2] M. B. Porch found that vanillin accelerates the peroxidase reaction of milk.

[3] Ber. d. chem. Ges., **40**, 230–235 (1907).

[4] *Ibid.*, **37**, 3785–3800 (1905).

[5] See Dupouy: Thèse, Bordeaux 1899, p. 43.

[6] J. de Physiol. et de Pathol. Gen., **4**, 442 (1902).

peroxidase activity of cows' milk is increased by this salt. Of the various substances whose effect on the peroxidase oxidation has been tested in this laboratory quite a number, including triiodophenol, cane sugar, maltose, formic aldehyde, glycin, malic and tartaric acids, etc., etc., have been found to slightly accelerate the oxidation. Whether these substances properly belong to the class of peroxidase accelerators or to class (2) can only be determined by further investigation.

To class (2) belong thymol, eugenol, guaiacol, benzoic acid, salicylic acid, tannin, and benzyl alcohol.

To class (3) belong, according to Hunger,[1] the tannins and certain sugars; certain substances ordinarily classed among the poisons, such as hydroxylamine, hydrazine, hydrocyanic acid and the cyanides, whose effect on the peroxidase reaction has recently been investigated by Bach;[2] and also acids and alkalies at certain concentrations. Catalase has also been found by Chodat and Pasmanik[3] to retard the oxidation of hydriodic acid by peroxidase and hydrogen peroxide.

It should be observed in this connection, however, that at present it is impossible to adopt any hard and fast classification of substances with regard to their effect on peroxidase oxidations for the reason that a given substance, which under certain conditions and at certain concentrations is without influence on the oxidation, may under other conditions and at other concentrations greatly accelerate it. Such a substance is resorcin, which under the conditions of our experiments has been found to be practically without influence on the peroxidase reaction of milk, whereas it has been found to greatly accelerate the oxidation of phenolphthalin by hydrogen peroxide and the peroxidase of horseradish. Our results show conclusively, however, that certain substances, especially certain compounds of the type of the phenols, do exert a markedly accelerating effect on

[1] Ber. d. botan. Ges., **19,** 374–377.
[2] Ber. d. chem. Ges., **40,** 3185–3191 (1907).
[3] Arch. Sci. Phys. Nat., **23,** 386–393 (1907).

such oxidations as are accomplished by hydrogen peroxide through the aid of a peroxidase. In my opinion, such substances act in the capacity of auxiliary oxygen carriers and are themselves oxidized more or less completely in such processes. That such is the case is indicated by the fact that most of them, at least, when acted on by hydrogen peroxide and a peroxidase exhibit characteristic color changes which other chemists, among them Bertrand,[1] Bourquelot,[2] Gillet,[3] and Bach,[4] have attributed to oxidation; and also by the fact that mixtures containing such substances, together with hydrogen peroxide and an active peroxidase, and which originally possess powerful oxidizing properties, soon lose their oxidizing power when heated or even allowed to stand for a short interval at ordinary temperature.

In the light of our present knowledge concerning the mechanism of oxidations accomplished by hydrogen peroxide under the influence of an oxygen carrier,[5] it seems reasonable to suppose that a peroxidase accelerates oxidations by hydrogen peroxide by reason of the fact that it forms a peroxide of some kind which is less stable than hydrogen peroxide itself and which therefore gives up its oxygen more easily than hydrogen peroxide to any oxidizable substance which may happen to be present.[6] Graphically, these changes may be represented in the following, in which P represents the peroxidase and B the peroxidase reagent:

$$(1) \ P + H_2O_2 \longrightarrow PO_2,$$

and

$$(2) \ PO_2 + 2B = 2BO + P,$$

or

$$(3) \ PO_2 + B = BO + PO.$$
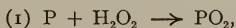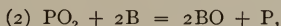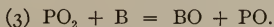
[1] Bull. Soc. Chim. [3], **11**, 717–721 (1894).
[2] Compt. rend., **123**, 315–317 (1896).
[3] J. de Phys. et de Path. Gen., **4**, 450 (1902).
[4] Ber. d. chem. Ges., **40**, 230–235 (1907).
[5] See Loevenhart and Kastle: This Journal, **29**, 397–437; and also Kastle and Loevenhart: *Ibid.*, **29**, 563–588 (1903).
[6] See Kastle and Loevenhart: This Journal, **26**, 564–566 (1901). This view regarding the mode of action of a peroxidase on hydrogen peroxide has been confirmed by the later work of Bach and Chodat; see Ber. d. chem. Ges., **37**, 1342–1348 (1904).

It is also well known that one peroxide may be formed from another by processes of ordinary double decomposition.[1] Hence it is readily conceivable that under certain conditions the peroxide resulting from the action of the hydrogen peroxide on the peroxidase might convert a second oxidizable compound, *viz.*, the auxiliary oxygen carrier, into a peroxide and that this in turn might accomplish the oxidation of another oxidizable substance, *viz.*, the peroxidase reagent (phenolphthalin, guaiacum, paraphenylenediamine, etc.), more readily than this could be accomplished by the peroxide resulting from the action of the peroxidase itself on the hydrogen peroxide. Graphically, these changes may be represented in the following, in which P represents the peroxidase, A, the auxiliary oxygen carrier, and B, the peroxidase reagent, that is, the substance whose oxidation is really under observation:

$$(1) \ P + H_2O_2 \rightleftharpoons PO_2$$

and

$$(2) \ PO_2 + A = P + AO_2,$$

or

$$(3) \ 2PO_2 + A = 2PO + AO_2,$$

and

$$(4) \ AO_2 + B = AO + BO.$$
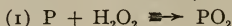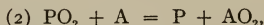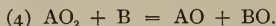
This view of the process enables us to understand the function of an auxiliary oxygen carrier in peroxidase oxidations and is capable of practically unlimited extension.

According to Engler[2] and others, hydrogen peroxide may result directly from the autoxidation of various substances containing labile hydrogen atoms, such as indigo white, etc., etc., and also by the hydrolysis of another peroxide, thus:

$$RO_2 + H_2O = RO + H_2O_2.$$
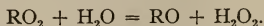
It might therefore be formed under certain conditions from

[1] See Engler and Weisberg: "Vorgänge der Autoxydation," Braunschweig, 1904, p. 31.

[2] *Ibid.*, 30–32.

an oxygenase, and as pointed out by Bach and Chodat,[1] hydrogen peroxide itself may play a definite rôle in the life of the cell. The universal distribution of catalase in living tissues and secretions would also seem to point to the formation of hydrogen peroxide in the respiratory process. According to Loew,[2] the function of catalase is to protect the living organism against the accumulation of hydrogen peroxide within the tissues. There can be no doubt, however, that while it would be largely decomposed into water and oxygen, under these conditions a part of it, at least, would probably be utilized in the oxidation of readily oxidizable substances, as a result of the action of the peroxidases; and in the light of the results described in the foregoing part of this communication, we can readily understand how, if hydrogen peroxide were ever formed in the living cell, it could be turned to immediate account for purposes of active and vigorous oxidation through the combined action of a peroxidase and a peroxidase accelerator. It is also readily conceivable that if certain substances accelerate oxidations accomplished by a peroxidase and hydrogen peroxide, they might also accelerate oxidations accomplished by means of a peroxidase and other peroxides, including the oxygenases. It also seems reasonable to suppose that among the great diversity of readily oxidizable substances met with in living tissues and in animal and plant secretions, a number would be found to greatly accelerate peroxidase oxidations. To take a case in point, Bertrand[3] found such a readily oxidizable substance in the sap of the lac tree, *viz.*, laccol, a substance which, according to this author, possesses the properties of a polyatomic phenol and whose oxidation by molecular oxygen, under the influence of laccase, gives rise to the black pigment of lac varnish. It, therefore, seems probable, in the light of what has been shown regarding the accelerating action of certain of the phenols on peroxidase oxidations, that laccol might also function as a peroxidase accelerator; and that

[1] Ber. d. chem. Ges., **35,** 1275–1279 (1902).
[2] Report No. 66, 1901, U. S. Dept. of Agriculture. Also Ber. d. chem. Ges., **35,** 2487–2488 (1902).
[3] Bull. Soc. Chim. [3], **11,** 717–721 (1894).

in its oxidation by laccase, as this occurs normally in the sap of the lac tree, it (laccol) could probably effect the oxidation of other less readily oxidizable substances. It would seem likely, therefore, that the peroxidase accelerators or auxiliary oxygen carriers are of considerable significance for biological oxidations. It is therefore my intention to continue these investigations in the hope of being able to throw further light on this particular phase of the subject.

WASHINGTON, D. C.,
March, 1908.

IMPROVEMENT IN CELLS FOR THE MEASUREMENT OF OSMOTIC PRESSURE.[1]

BY H. N. MORSE AND B. MEARS.

Progress has recently been made in the development of the method for the measurement of osmotic pressure which has contributed materially to the accuracy of the results and the convenience of the work. The improvements have been principally along the three following lines: (1) cell construction and management; (2) the calibration, comparison, and verification of manometers; and (3) the maintenance of constant bath temperatures. All of these are matters of first class importance, and it is thought advisable to devote a short paper to each of them. The present paper deals with improvements in cells.

It is now nearly nine years since the work upon osmotic pressure was begun in this laboratory, and probably more than half of all the time given to the subject has been devoted to experimental work in cell construction. Notwithstanding so much effort, we have been unable, until recently, to provide ourselves with an adequate supply of faultless cells. By "faultless" cells, we mean those in which the solutions systematically develop their maximum pressures. Some account[2] has already been given of the earlier difficulties which

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425, and 558; **38**, 175; **39**, 667; **40**, 1 and 194.

[2] THIS JOURNAL, **34**, 1.

led us to abandon the coöperation of the potters and to attempt to work out the problem of cell making in the laboratory. The problem has proved to be a hard one, and at the present time it is only partially solved. It has long been known that to insure success the pores of the cell wall must be excessively small, and that the porosity must be very uniform throughout, also that the cells must stand burning at very high temperatures without becoming entirely nonporous. But we are still unable to say precisely how all these and still other essential qualities may be secured without any large proportion of failures. During the first five years, we produced about a dozen good cells. Recently about one cell in four has proved to be satisfactory. It is not our purpose, however, to discuss in this paper the problem of cell making, because we are still far from having solved it. We wish, rather, to deal with the form of the cell and the methods of closing it for the measurement of pressure.

Figure 1 (reproduced from a former paper[1]) represents the cell which was employed in the earlier work, and which, with certain modifications, is still used to some extent. Its construction and the purpose of the different parts are sufficiently obvious, so that it is necessary only to call attention to its weak points.

The membrane, when once deposited on the cell wall, must not be subjected to any strain except that exerted directly outward by the osmotic pressure; in other words, it must not be disturbed by any of the operations connected with the closing and opening of the cell. To avoid this, the glass tube, B, was rigidly fixed in the cell, A. The lower end of the glass tube was accurately ground to fit the soapstone ring, b. In order to prevent the solution from penetrating the cement above, and at the same time to protect the latter from liquid entering through the exterior wall, the glass tube and the soapstone ring were joined together watertight by means of molten shellac, and the lower end of the tube and ring, and also the whole wall of the cavity, were painted with a solution of rubber. The ring and tube were then pressed

[1] THIS JOURNAL, **34**, 4.
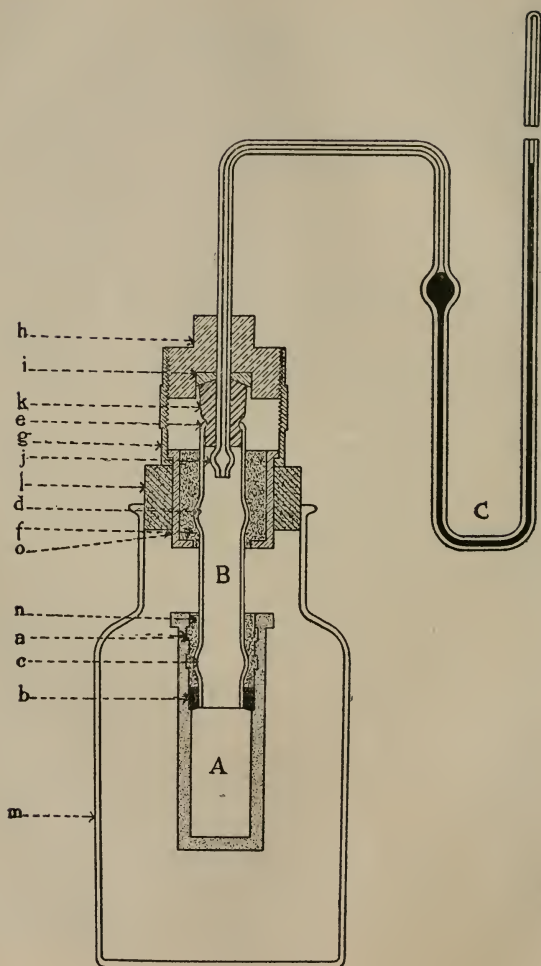
Fig. I.

into place, and the space between the former and the cell wall was filled with the dissolved rubber, after which the rubber lining was hardened by baking at a temperature below the melting point of the shellac. Finally, the space above the ring was filled with the litharge-glycerine cement.

So far as securing a rigid union of glass tube and cell is concerned, the method proved to be perfectly satisfactory; but two difficulties developed, either of which made necessary an occasional reopening and renovation of the cell, and these, as explained in a former paper,[1] are tedious and often unsuccessful operations. After a few months of use, the cell was sure to fail in consequence of a peeling of the rubber from some of the parts protected by it. Again, the membrane becomes, in the course of time, so dense and thick that the passage of water through it is intolerably slow, and it is necessary then to remove it and substitute a thinner one. This cannot be done without opening the cell. The removal of the membrane requires some caution. If it is attempted to dissolve it in strong reagents, like the concentrated mineral acids, the cell wall is sure to be ruined so far as the deposition of a new membrane is concerned. The disadvantages of a compound cell, *i. e.*, one which, like that in the figure, is made up of separate parts which must be securely united, were found to be so great that much time has been spent in devising and testing simpler forms; but before entering upon a description of the new cell, we wish to explain certain other defects of the older one.

It will be seen in the figure that the upper end of the glass tube is considerably contracted; and it is obvious that a great deal of difficulty must be experienced in working the material of the rubber stopper through the small hole at the top into the wider tube below, and also in providing for the escape of solution in order to make room for the entering stopper. The implement which served for both purposes has already been described. It consists of a long piece of round steel with one tapering end, which is bent to a hook form and furrowed out on the underside. The same tool is employed

[1] THIS JOURNAL, **37**, 325.

in opening the cell, both to admit air and to assist in working the stopper out of the tube. The manipulation in closing and opening such a cell is the most difficult part of the whole work, and it can be entrusted only to the most experienced.

The conduct of the rubber stopper under pressure was responsible for much of the uncertainty pertaining to the earlier measurements, and we propose to explain the difficulties which arose in connection with it and how they were overcome. In the first place, the enlargement on the end of the manometer, j, was driven upwards into the stopper, spreading it and forcing some of the material through the contracted end of the glass tube, e. These movements have frequently been spoken of as "manometer displacement" and "distortion of the stoppers." The effect of them is, of course, to increase the capacity of the cell, and consequently, to dilute the solution. The crowding of the manometer into the stopper was soon overcome by tying the latter very tightly with shoemakers' thread just above the enlargement on the former. But this did not prevent the forcing of some of the material of the stopper out of the glass tube into the space above, that is, the distortion of the stopper continued, though there was no longer any slipping of the manometer. The obvious remedy was to render perfectly rigid the portion of the stopper which is outside of the glass tube, and the simplest device for this purpose was found to be the most effective one. After the stopper had been worked into the cell to the required depth, the whole of the projecting portion, k, was tightly wound with waxed shoemakers' thread, with the result that we were no longer troubled with manometer displacement or distortion of stoppers.

The dilution of the cell contents due to the upward movement of the manometers and of the material of the stoppers was considerable in the first three series of measurements, but in the later ones it was quite negligible, when compared with other sources of dilution for which the rubber stopper is in a large measure responsible. The closing of the cell occupies considerable time, usually from 10 to 15 minutes, and it is clear that during this time the contents of the cell

are under a mechanical pressure which is less than the osmotic pressure, and that water must enter from the wet cell wall over the whole surface of the membrane. The rate of the inflow of water depends upon the difference between the mechanical pressure which is exerted at the stopper and the osmotic pressure of the solution, hence in closing the cell, the operator who holds it and manipulates the manometer endeavors to maintain upon the solution as high and as continuous a mechanical pressure as possible. A more effective remedy, however, for the inflow of water at this period is the practice, employed throughout the later series of measurements, of dipping the cell, before closing, in a solution whose concentration is equal to, or slightly greater than that of the solution within the cell. The dilution of the solutions during the closing period was doubtless considerable in the first three series of measurements. In the later series, it is not believed to have affected seriously the accuracy of the results.

When the cell is to be opened, the hook of the steel implement is inserted between the glass and the rubber in order to relieve the pressure by admitting air to the solution, and the stopper is then slowly withdrawn by twisting it around in the glass tube. Unfortunately, the hook cannot be allowed to remain in place while the stopper is being removed. The form of the tube at the end and the danger of cracking the glass make it necessary to withdraw the instrument after each admission of air, before the work of removing the stopper can be resumed. Hence the contents of the cell are frequently under diminished pressure during the opening period, and the necessary result of this condition is an increased inflow of water from the cell wall. The dilution of the cell contents due to diminished pressure can also be lessened by "dipping," but it cannot be altogether prevented by this means.

The perplexities regarding the proper correction of the results for loss in rotation, which are created by the fact that dilution during the closing period precedes the measurement, while that which occurs during the opening period is subsequent to the measurement of pressure, have already been

discussed at length in former papers, and they need not be reconsidered in a paper in which it is intended to deal with matters of method rather than with results.

The dilution of the cell contents during the opening period was finally overcome by a very simple device, namely, by driving through the stopper, parallel to the manometer tube, a fine hollow steel needle, which was left in place until the manometer and cell had been separated. The solution was thus brought under atmospheric pressure and continued so to the end of the operation. The use of the hollow needle does not alone suffice to prevent all dilution, for it is obvious that with a solution and water on opposite sides of a membrane, the latter must pass into the former as long as the pressure on the solution is less than its osmotic pressure. But when the use of the needle was supplemented by "dipping," it was found that there was in most cases no dilution whatever of the cell contents, in other words, that the solutions, as a rule, suffered no loss in rotation while in the cells.

A serious difficulty with the old form of cell arises from the fact that the time required for closing it is quite long, and that it must be held in the warm hand throughout the operation. The ill consequences of this are twofold; in the first place, our experience has shown us that the good conduct of a membrane depends very much upon the maintenance of a constant temperature from the time of its deposition to the end of the measurement of pressure. On that account, it has been our practice to deposit or repair the membrane at the temperature at which the measurement is to be made, and thereafter to maintain the cell at that temperature until the experiment is finished. Again, if the solution is expanded by holding the cell in the warm hand, and, while it is in that condition, the cell is closed—fixing its capacity—the subsequent fall in temperature in the bath is attended by a dilution of the solution. The custom of wrapping the cell in nonconducting material and of wearing a glove upon the hand which holds it, or of frequently dipping the hand in cold water, is an uncertain remedy for the difficulties which have

been enumerated; the true remedy is a cell which can be more quickly closed.
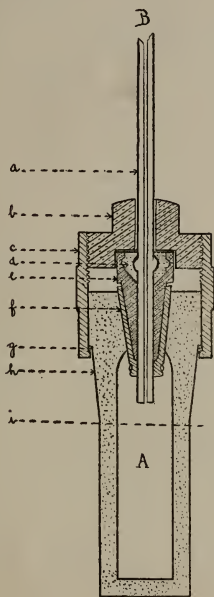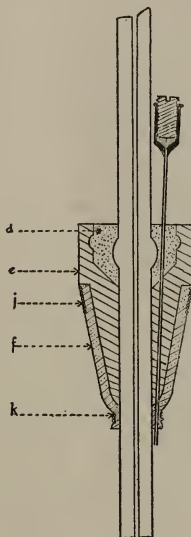
Fig. II.   Fig. III.

Fig. II. represents a new form of cell which is entirely free from the objectionable features of the older one. The upper end of the cell is glazed, inside and out, to the line, i, or to any other depth, according to the area which the membrane is required to have. In some cases, where it was desired to experiment with very small membranes—as will doubtless be necessary with the electrolytes—the whole cell was covered with the glaze, which was afterwards ground away over and under the spot on which the membrane was to be deposited. Considerable difficulty was experienced in securing a suitable glaze. We first tried a material which is used by the potters

on the better class of tableware. But this was found to "craze" badly when applied to our cells, showing that its expansion coefficient was too small. However, by gradually adding silica and feldspar to the potters' material, we finally obtained a glaze which was continuous and which did not crack when subjected to sudden changes of temperature.

After baking, and before glazing, the cell is placed in the lathe, and the upper end of it is "shaped up" with a carborundum grinder. The conical opening is ground to a true taper, and the outside of the cell is cut down to fit the brass collar, *c*.

The brass cone, *e* (Figs. II. and III.), is firmly attached to the manometer by means of Wood's metal, *d*. The rubber cap, *f*, is slipped over the brass cone, *e*, and securely tied at its two extremities (*j* and *k*, Fig. III.). The tying of the rubber at *k* with twisted shoemakers' thread, and the hard pressing of the rubber above between the conical brass and porcelain surfaces do not alone suffice to prevent a difficulty which was experienced with the old form of cell. The portion of the rubber which is not forced into the cell must be rigidly supported, otherwise there is a slow upward movement of the rubber below, and a condition is created which is quite analogous to the "distortion" of the stopper in the old cell. The manometer cannot "rise" in this case, but the capacity of the cell is increased by the gradual upward movement of that portion of the rubber which is under greatest pressure, and this is followed by a dilution of the solution. For this reason, the upper end of the rubber cap (*j.*, Fig. III.) is tightly wound with waxed shoemakers' thread, and it is quite essential to continue the winding so far down that no unsupported rubber is left above the top of the cell, that is, the wound portion must extend somewhat into the neck of the cell.

The closing of the new cell is a very simple operation which may be finished in less than a minute. A fine hollow steel needle is placed between the rubber, *f*, and the wall of the cell to provide for the escape of superfluous solution. The brass nut, *b* (Fig. II.)—which is slotted so that it may be readily separated from the manometer, and also to make room

for the needle—is placed in position and held with a wrench while the brass collar, *c*, is slowly turned with the hand.   When the manometer has been made sufficiently firm in its place, the needle is withdrawn, and the turning of the collar is continued until the required amount of "initial" pressure has been produced.

The opening of the cell is equally easy and expeditious. The collar is turned in the reverse direction until the nut can be removed.   If the manometer is not wholly released by this operation, the sharp pointed hollow needle is driven in through the rubber, or between it and the neck of the cell, after which, the manometer and cell can be separated without fear of subjecting the solution to diminished pressure.

In order to protect the cell from injury by the turning brass collar, a ring of lead is inserted between them at *g*.   A less rigid material, like rubber, leather, or "fiber," cannot be employed for this purpose, because any gradual decrease in the vertical thickness of the ring is attended by a corresponding upward displacement of the manometer.

The practice of "dipping" is also employed in connection with the new cells, notwithstanding the fact that the solutions are never under less than atmospheric pressure.   The reason for continuing the custom will be clear when it is recalled that dilution of the solution in the cell must ensue whenever the pressure upon it is less than its potential osmotic pressure.

The procedure just described requires a certain amount of good judgment as to the proper time for removing the needle when a cell is being closed.   Moreover, it is sometimes found that the needle is withdrawn with difficulty when the manometer is firmly fixed in its place in the cell.   Good judgment is especially necessary in the case of dilute solutions.   If the needle is prematurely withdrawn, it will be found that screwing down to maximum permissible "initial" pressure does not suffice to fix the manometer firmly in its place.   It is not allowable, as a remedy in such cases, to establish an initial pressure which is greater than the osmotic pressure, because this always produces a concentration of the solution, and, consequently, an abnormally high osmotic pressure.   The

reason is quite obvious, and our experience emphasizes the fact that *the mechanical pressure upon the solution must never exceed the maximum osmotic pressure.* We have no hesitation in affirming again that it is a mistake to suppose that osmotic pressure can be measured by increasing the mechanical pressure until it is in equilibrium with the osmotic pressure, or by raising the former above the latter and then waiting for equilibrium to establish itself.

Fig. III. shows a disposition of the needle which is especially advantageous for dilute solutions, and which is not objectionable in the case of concentrated ones. The needle, as indicated in the figure, is permanently fixed in the brass piece, *f*, and provision is made at the top for permitting or stopping, at will, the outflow of solution from the cell. The upper end of the needle is shown on a larger scale in Fig. IV.

Fig. IV.

We have also succeeded, after considerable trouble, in making a cell similar to the one described, which does not require glazing—one in which the upper half is a dense and water-tight porcelain, while the lower half is porous and in every way suited to the deposition of a membrane. The problem to be solved was, of course, so to shade the two different clays through a certain distance in the middle of the cell

that there could not be an abrupt change in expansion coefficient at any point between the porcelain above and the porous part below.

JOHNS HOPKINS UNIVERSITY,
May 29, 1908.

VISCOSITY AND FLUIDITY.

[PRELIMINARY PAPER.]

BY EUGENE C. BINGHAM.

Efforts have been made in earlier papers[1] to show that the fluidities of liquid mixtures are normally a linear function of the composition of the mixture. In investigating pure liquids, it is now found that for unassociated substances, the fluidities are approximately a linear function of the temperature of the substance. This relation may be expressed by the formula

$$t_1 = A\phi + K_1 \tag{1},$$

where t is the temperature absolute, ϕ the fluidity, and A and K_1 are constants. But associated compounds, the alcohols especially, depart widely from the linear type. At high temperatures their fluidities approximate the linear type, but at low temperatures the fluidity curves do not reach a zero value, but appear to approach the zero value asymptotically, as already predicted by Bousfield and Lowry[2] and by Kohlrausch.[3] To represent the increase in temperature required to give the fluidity ϕ on account of the association of the substance, use is made of the expression

$$t_2 = K_2 - \frac{B}{\phi} \tag{2},$$

where B and K are constants. Adding together these two equations, we have

$$t = t_1 + t_2 = A\phi - \frac{B}{\phi} + C \tag{3}.$$

[1] *Cf.* THIS JOURNAL, **34**, 481 (1905); Z. physik. Chem., **57**, 193 (1906); Carnegie Institution Publication No. **80**, 107 (1907); THIS JOURNAL, **35**, 195 (1906).
[2] P. Roy. Soc., **71**, 42 (1902).
[3] *Ibid.*, **71**, 338 (1903).

For many purposes it is highly desirable to have an equation with no more than three constants. Thorpe and Rodger, in their classic investigation,[1] limited themselves to equations with but three constants, and they finally adopted Slotte's equation,[2]

$$\eta = \frac{c}{(a + t)^n},$$

as the best equation at their disposal with which to represent viscosity data. Hence, the above equation (3) must be used to compare with Slotte's equation. Too much, however, must not be expected from it, because it neglects to consider the fact that as the number of particles is increased by the breaking down of association, these new particles also contribute to the increase in fluidity in a linear manner. An approximate equation containing four constants (a larger number of constants than this renders the equation unwieldy) is

$$t = A\phi - \frac{B}{\phi + D} + C \qquad (4).$$

The extremely accurate data of Thorpe and Rodger naturally served as a basis for testing the above equations. Eliminating the highly associated classes of substances, acids, alcohols, and water, the results obtained for the 68 remaining substances examined by them are given by equation (3) with an average difference of only 0.08 per cent. Slotte's equation for the same substances, as far as they gave the data, result in an average difference for 58 substances of 0.14 per cent. If the acids, alcohols, and water are included in the test of equation (3), then the average difference for 87 substances rises to 0.17 per cent. The highest average difference is 1.17 per cent in the case of active amyl alcohol. Slotte's equation did not hold at all for many of these, in one case, the equation calculated for one part of the curve giving a difference of over 800 per cent at another part of the curve. It may be remarked here that practically a thousand duplicate observations are at the basis of the above average.

[1] Phil. Trans. [A], **185**, 307 (1894), and **189**, 71 (1897).
[2] Beibl., **16**, 182 (1892).

The following table for hexane will serve to exemplify the above agreement:

ϕ.	Temperature observed.	Temperature calculated.	Per cent difference.	Per cent difference. T. & R.
254.39	273.80	273.80	0.00	—0.03
279.2	282.15	282.44	+0.10	+0.17
296.0	287.75	287.97	+0.07	+0.09
312.3	292.98	293.14	+0.05	+0.07
329.5	298.39	298.43	+0.01	—0.03
345.54	303.23	303.24	+0.00	—0.03
367.3	309.76	309.59	—0.05	—0.11
391.2	316.47	316.28	—0.06	—0.04
404.9	320.42	320.09	—0.10	—0.16
425.3	325.90	325.67	—0.07	—0.09
448.2	331.76	331.77	+0.00	+0.05
466.64	336.59	336.61	+0.01	0.00

Average per cent difference: equation (3), 0.04; Thorpe and Rodger, 0.07. Constants in equation (3): $A = 0.21892$, $B = 9137.8$, $C = 254.03$.

In testing associated substances by means of equation (4) the agreement with the observed values is equal to that with the simpler equation (3) and unassociated substances. Of course, equation (4) may be used in the case of those substances also, wherever the agreement is not already within the limits of experimental error. Active amyl alcohol gives an average difference of 1.17 per cent with equation (3). With equation (4) this becomes only 0.08 per cent.

Duff[1] has recently given equations with four constants which seem to give closer agreement than any heretofore proposed. The equations are somewhat unwieldy and have not been applied to many substances, so an extensive comparison cannot be made. The average difference obtained by Duff between the observed and the calculated values is as follows: for isobutyl alcohol, 0.35 per cent; for dimethylethylcarbinol, 0.24 per cent; and for water, 0.18 per cent. Equation (4) gives for these an average difference of 0.09, 0.08, and 0.01 per cent, respectively. The following table shows the nature of this agreement in the case of water.

[1] Physic. Rev., **4**, 404 (1896).

ϕ.	Temperature observed.	Temperature calculated.	Per cent difference.	Per cent difference. T. & R.	Per cent difference. Duff.
56.91	273.37	273.37	0.00	+0.2	+0.3
58.48	274.13	274.17	+0.01	+0.2	+0.3
62.19	276.09	276.02	—0.02	+0.1	—0.2
65.15	277.47	277.47	0.00	0.0	0.0
66.93	278.45	278.33	—0.04	0.0	+0.4
72.62	281.01	281.02	+0.00		
84.67	286.53	286.48	—0.02	+0.2	—0.4
104.71	295.02	294.93	—0.03	—0.4	—0.4
127.23	303.72	303.68	—0.01	—0.2	—0.1
151.06	312.32	312.32	0.00	0.0	0.0
173.61	320.03	320.03	0.00	+0.2	+0.2
199.60	328.53	328.48	—0.02	+0.2	+0.2
226.50	337.01	336.85	—0.05	+0.1	+0.1
255.43	345.54	345.51	—0.01	+0.4	+0.4
283.69	353.75	353.71	—0.01	+0.3	+0.1
315.96	362.90	362.81	—0.02	0.0	0.0
346.02	371.09	371.09	0.00	0.0	0.0
353.35	373.00	373.08	+0.02	0.0	0.0

Average per cent difference: equation (4), 0.01; Thorpe and Rodger, 0.15; Duff, 0.18. Constants in equation (4): $A = 0.23275$, $B = 8676.8$, $C = 309.17$, $D = 120$.

RICHMOND COLLEGE, RICHMOND, VA.,
    March 19, 1908.

UREIDES AND CYANAMIDES OF THE DIALKYLOXY-ACETIC ACIDS.

By ERIK CLEMMENSEN AND ARNOLD H. C. HEITMAN.

The ureides of the oxy-fatty acids are represented only by the hydantoins, $C_nH_{2n}\begin{smallmatrix}NH.CO\\|\\CO.NH\end{smallmatrix}$, and the hydantoic acids, $C_nH_{2n}\begin{smallmatrix}NH.COOH\\CO.NH_2\end{smallmatrix}$, while the real ureides,

$C_nH_{2n}\begin{smallmatrix}OH\ NH_2\\CO—NH\end{smallmatrix}CO$ and $\begin{smallmatrix}C_nH_{2n}\begin{smallmatrix}OH\\CONH\end{smallmatrix}\\CO,\\C_nH_{2n}\begin{smallmatrix}CONH\\OH\end{smallmatrix}\end{smallmatrix}$
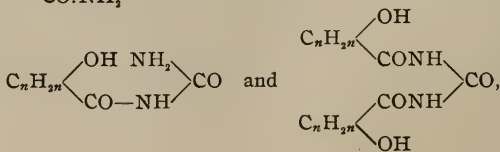
have not been made. By real ureides of the oxy-fatty acids we understand compounds formed by substituting one or more of the hydrogen atoms in ureas with the radicals of the oxy-fatty acids, $C_nH_{2n}\begin{cases} OH \\ CO— \end{cases}$. Hence these compounds will still contain the characteristic alcoholic hydroxyl groups, and their C_nH_{2n} groups will not be linked directly to the nitrogen atoms as in the hydantoins and the hydantoic acids. We therefore thought it would be of interest to try to prepare them and study their properties.

For several reasons we started with the dialkyloxyacetic acids, and this paper will deal exclusively with these; but we have already begun the work on some of the other oxy-fatty acids, especially the glycollic and the lactic acids, the result of which we intend to publish later.

Errera[1] has prepared and described the *C*-dialkylhydantoins,

$$R_2C\begin{cases} NH . CO \\ \quad\quad | \\ CO . NH \end{cases},$$
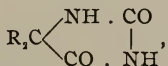
whereas the real *C*-dialkyloxyacetylureides,

$$R_2C\begin{cases} OH \quad NH_2 \\ CO — NH \end{cases}CO \quad \text{and} \quad \begin{matrix} R_2C\begin{cases} OH \\ CO.NH \end{cases} \\ R_2C\begin{cases} CO.NH \\ OH \end{cases} \end{matrix}CO,$$
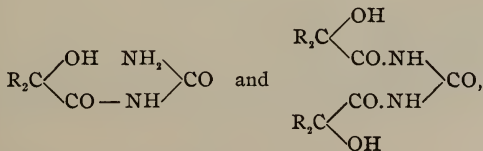
as already mentioned, have not been made before. A. Michael[2] obtained malonylurea by condensing diethyl malonate and urea by means of sodium alcoholate, and E. Fischer and A. Dilthey[3] have made the *C*-dialkylmalonylureides in practically the same way. We, therefore, had every reason to expect a good result by using this method in making the *C*-dialkyloxyacetylureides, and this was entirely confirmed, for by treating

[1] Gazz. chim. ital., **26**, I, 197.
[2] J. prakt. Chem. [2], **35**, 456.
[3] Ann. Chem. (Liebig), **335**, 334.

the esters of the dialkyloxyacetic acids with urea and sodium alcoholate, we obtained ureides of the formula

$$R_2C\begin{array}{c} \diagup OH \\ \diagdown CONH \end{array}\diagdown_{CO,} \diagup_{CONH}$$
$$R_2C\begin{array}{c} \diagup \\ \diagdown OH \end{array}$$

the following reaction taking place:

$$R_2C\begin{array}{c}\diagup OH\\\diagdown COOC_2H_5\end{array} + \begin{array}{c}H_2N\diagdown\\ \diagup CO\\H_2N\end{array} + \begin{array}{c}NaOC_2H_5\\ \\NaOC_2H_5\end{array} =$$
$$R_2C\begin{array}{c}\diagup\\\diagdown COOC_2H_5\end{array}$$
$$R_2C\begin{array}{c}\diagdown OH\end{array}$$

$$R_2C\begin{array}{c}\diagup OH\\\diagdown CONNa\end{array}\diagdown_{CO} + 4C_2H_5OH.$$
$$\diagup_{CONNa}$$
$$R_2C\begin{array}{c}\diagdown OH\end{array}$$
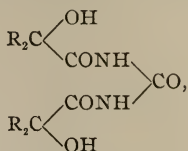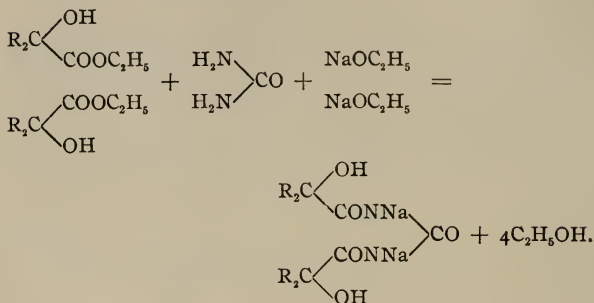
The reaction takes place at water bath temperature with a highly satisfactory yield.

On the other hand, although we varied the process in many ways, we were not able to obtain the ureides of the type,

$$R_2C\begin{array}{c}\diagup OH \quad NH_2\diagdown\\\diagdown CO—NH\diagup\end{array}CO,$$
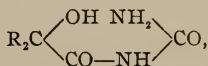
corresponding to urea in which only one of the hydrogen atoms has been substituted with the acid radical.

The new ureides are low melting, very stable substances which can be distilled under reduced pressure without decomposition. They act as rather strong dibasic acids.

Michael[1] obtained malonylthiourea and malonylguanidine by using thiourea or guanidine in his process instead of urea,

[1] J. prakt. Chem. [2], **35,** 456.

and the thioureides and guaneides of the dialkylmalonic acids were prepared in a similar way by Fischer and Dilthey.[1] However, when we tried to make the thioureides and guaneides of the dialkyloxyacetic acids by treating the esters and thiourea or guanidine with sodium alcoholate, we came to a very different result, as in both cases we obtained the same dialkyloxyacetylcyanamides, $R_2C\genfrac{}{}{0pt}{}{OH}{CO.NH.CN}$, compounds which have not hitherto been made.

No doubt, in the presence of the dialkyloxyacetic esters the sodium alcoholate converts the thiourea and the guanidine into sodium cyanamide:

$$C(NH)\genfrac{}{}{0pt}{}{SH}{NH_2} + NaOC_2H_5 =$$

$$C\genfrac{}{}{0pt}{}{\diagup\!\!\!\!\!= N}{NHNa} + H_2S + C_2H_5OH ;$$

$$C(NH)\genfrac{}{}{0pt}{}{NH_2}{NH_2} + NaOC_2H_5 =$$

$$C\genfrac{}{}{0pt}{}{\diagup\!\!\!\!\!= N}{NHNa} + NH_3 + C_2H_5OH ;$$
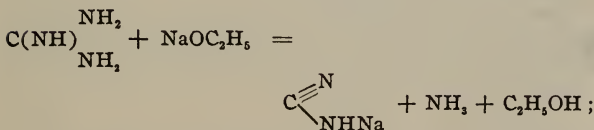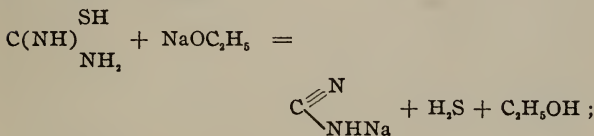
and the sodium cyanamide formed reacts in turn with the esters, forming the dialkyloxyacetylcyanamides:

$$R_2C\genfrac{}{}{0pt}{}{OH}{COOC_2H_5} + \genfrac{}{}{0pt}{}{N}{HNaN}\!\!\diagdown\!\!C =$$

$$R_2C\genfrac{}{}{0pt}{}{OH}{CO.NNa.CN} + C_2H_5OH.$$
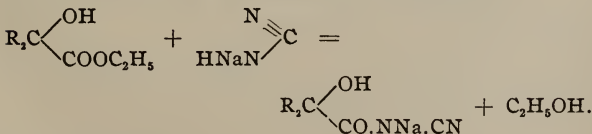
The whole reaction, which takes place on treating a mixture of the dialkyloxyacetic esters and thiourea or guanidine with sodium alcoholate, is therefore as follows:

$$R_2C.OH.COOC_2H_5 + CS(NH_2)_2 + 2C_2H_5ONa =$$
$$R_2C.OH.CO.NNa.CN + NaSH + 3C_2H_5OH.$$
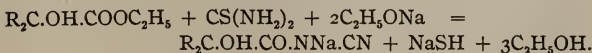
[1] Ann. Chem. (Liebig), **335**, 334.

We are unable to explain why this reaction takes place here, while the dialkylmalonic esters under the same conditions yield the thioureides and guaneides, but the hydroxyl groups no doubt play an important rôle, and further investigation, which we hope to carry on in the near future, will show whether or not this reaction is general for the oxy-fatty acids. As it seemed to us of considerable interest to ascertain whether the dialkylmalonylcyanamides could possibly be formed in this way, we repeated the experiments of Fischer and Dilthey with several modifications, but in all cases, however, we obtained the thioureides and the guaneides. In this connection we might remark that the low yield of diethylmalonylthiourea which Fischer and Dilthey[1] obtained possibly was due to the high temperature and the large excess of sodium alcoholate they employed, since on boiling an alcoholic solution of one molecule thiourea and one molecule diethylmalonic diethyl ester with two molecules sodium alcoholate, the yield of diethylmalonylthiourea exceeded 80 per cent of the theoretical.

The new cyanamides are high melting, well crystallizing substances, which by boiling with acids or alkalies are quantitatively converted into the *C*-dialkyloxyacetylureides, the following reaction taking place:

$$2R_2C{<}^{OH}_{CO.NH.CN} + 3H_2O =$$

$$R_2C{<}^{OH}_{CO.NH}{>}CO + 2NH_3 + CO_2.$$
$$R_2C{<}^{CO.NH}_{OH}$$
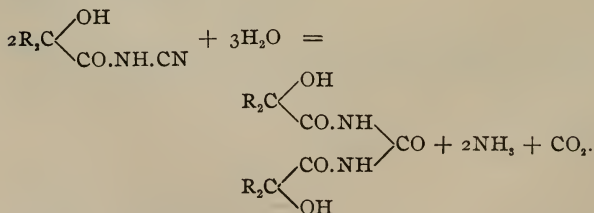
Since, therefore, we were unable to form the *C*-dialkyloxyacetyl thioureides and guaneides in this way, we tried several other methods, letting, for instance, phosphorus haloids and similar condensing agents act on mixtures of the acids and thiourea or guanidine, but without success, probably on account of the great tendency of the oxyacids to form anhydrides in the

[1] Ann. Chem. (Liebig), **335**, 350.

presence of these bodies, and it was by heating a mixture of diethyloxyacetic acid and thiourea to 180° that we first succeeded in obtaining *C*-diethyloxyacetylthiourea, the following reaction taking place:

$$(C_2H_5)_2C \underset{COOH}{\overset{OH}{<}} + \underset{H_2N}{\overset{H_2N}{>}}CS =$$

$$(C_2H_5)_2C \underset{CO.NH}{\overset{OH}{<}} \quad (C_2H_5)_2C \underset{CO.NH}{\overset{CO.NH}{>}} CS + 2H_2O.$$

$$(C_2H_5)_2C \underset{OH}{\overset{CO.NH}{<}}$$
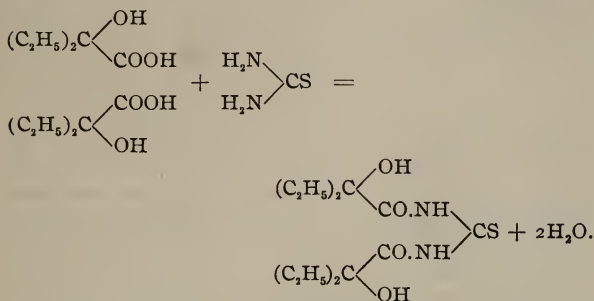
At the same time, however, another reaction takes place, as the alcoholic hydroxyl group takes part in the reaction, causing the formation of another compound hitherto unknown, namely, *C*-diethylthiohydantoin, and this secondary reaction predominates when the temperature is raised to 200° and an excess of thiourea is used. Thiourea must here react as follows:

$$(C_2H_5)_2C \underset{COOH}{\overset{OH}{<}} + \underset{H_2N}{\overset{HS}{>}}C.NH =$$

$$(C_2H_5)_2C \underset{CO.NH}{\overset{S—C.NH}{<}}{\overset{|}{}} + 2H_2O:$$
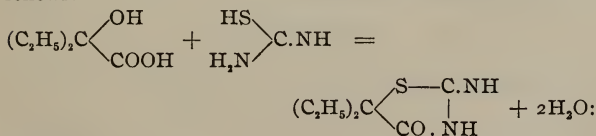
since the *C*-diethylthiohydantoin formed is converted by boiling with barium hydroxide into *C*-diethylthioglycolamide,

$$C(C_2H_5)_2 \underset{CO.NH_2}{\overset{SH}{<}},$$
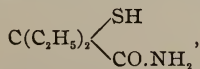
and by prolonged boiling into diethylthioglycollic acid,

$$C(C_2H_5)_2 \underset{COOH}{\overset{SH}{<}},$$
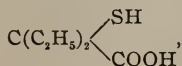
two compounds which have not been made before, the following reactions taking place:

$$(C_2H_5)_2C \underset{CO.NH}{\overset{S——C.NH}{\Big\langle}} \overset{|}{} + 2H_2O =$$

$$(C_2H_5)_2C \underset{CO.NH_2}{\overset{SH}{\Big\langle}} + CO_2 + NH_3 ;$$

$$(C_2H_5)_2C \underset{CO.NH_2}{\overset{SH}{\Big\langle}} + H_2O = (C_2H_5)_2C \underset{COOH}{\overset{SH}{\Big\langle}} + NH_3.$$
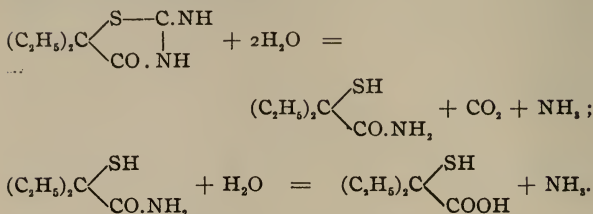
Unfortunately we did not have enough of the two substances, which we have designated as diethylthioglycollic acid and diethylthioglycolamide, to make a complete analysis. However, as the sulphur and nitrogen determinations gave results in full accordance with the theory, we do not doubt that these formulas are correct. It is furthermore in accordance with the results of Andreasch,[1] who found that the ordinary thiohydantoin, by boiling with baryta, yielded thioglycollic acid. The intermediate product, thioglycolamide, was, however, not formed in his case. We hope to be able to carry out a closer examination of all these thio compounds and to give the results in a later paper.

EXPERIMENTAL.

C-Diethyloxyacetylurea, $(C_2H_5)_2C.OH.CO.NH \Big\rangle CO.$ —The ethyl $(C_2H_5)_2C.OH.CO.NH$
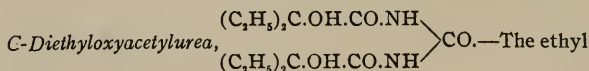
diethyloxyacetate we used was made by Fittig's modification[2] of Frankland and Duppa's process,[3] according to which one molecule ethyl oxalate and two molecules ethyl iodide are heated with an excess of granulated, slightly amalgamated zinc and small quantities of zinc ethyl and ether. The addition of zinc ethyl is inconvenient, and in our opinion not at all necessary. Our experience is that the yield depends mostly on the physical condition of the zinc, the spongy,

[1] *Ber. d. chem. Ges.*, **12**, 1385.
[2] *Ann. Chem.* (Liebig), **200**, 21.
[3] *Ibid.*, **126**, 109.

impure zinc which can be obtained on the market giving the best results. This was treated a short time with dilute sulphuric acid, then washed, dipped a few minutes in a 0.1 per cent solution of mercury chloride,[1] then washed carefully again and dried. By using equal parts of the nonamalgamated zinc (treated with sulphuric acid) and the amalgamated zinc, we obtained over 90 per cent of the theoretical yield. The ester boiled at 173°–175°.

In order to prepare the ureide, 5 grams sodium were dissolved in 100 cc. absolute alcohol, and to the cooled solution were added 32 grams ethyl diethyloxyacetate and 7 grams urea, care being taken to have both the materials and apparatus perfectly dry. The whole was then boiled in a flask with reflux condenser for about 5 hours. The reaction product, containing the sodium salt of the diethyloxyacetylurea, was slightly acidified with dilute hydrochloric acid, the alcohol distilled off, and the ureide, which formed an oily layer on top of the salt solution, separated from this, washed with a little cold water, dried, and then distilled *in vacuo*. A little water and ester first passed over and then the ureide at 175° under 20 mm. pressure. After a second distillation the whole amount of substance boiled constantly at 174°–176° under 20 mm. pressure. The yield was 25 grams, which is about 87 per cent of the theoretical.

The ureide thus obtained is a colorless, oily liquid, having a specific gravity of 1.1107 at 15°. At first we were not successful in our various efforts to crystallize it.

0.1899 gram substance gave 0.3750 gram CO_2 and 0.1363 gram H_2O.

0.1880 gram substance gave 16.5 cc. N at 28° and 751 mm.

	Calculated for $C_{13}H_{24}N_2O_5$.	Found.
C	54.17	53.86
H	8.33	7.98
N	9.72	9.52

The ureide probably still contained small quantities of impurities, and as we thought that these might prevent it from crystallizing, we tried to purify it further. The substance was

[1] Ann. Chem. (Liebig), **200**, 21.

boiled with magnesia, and the filtrate, containing the magnesium salt, precipitated with silver nitrate. The silver salt was collected, washed with cold water, and recrystallized from boiling water, again washed, and dried. The dry salt was dissolved in absolute alcohol, decomposed with hydrogen sulphide, and the filtrate from the silver sulphide freed from alcohol by evaporation. On leaving the remaining colorless oily liquid over sulphuric acid, it solidified to a mass of long, needle shaped, colorless crystals, which begin to soften at 28° and melt at 30°–31°. The substance was again converted into the silver salt, and this treated in the manner described above. The resulting substance had the same melting point, 30°–31°.

0.2575 gram substance gave 0.5106 gram CO_2 and 0.1897 gram H_2O.

0.3012 gram substance gave 27.1 cc. N at 26° and 747 mm.

	Calculated for $C_{18}H_{24}N_2O_5$.	Found.
C	54.17	54.08
H	8.33	8.19
N	9.72	9.81

Instead of the silver salt the mercury salt may be used. When once in possession of a crystal, it is not necessary to use the silver salt to get the ureide in the crystalline form, as the distilled substance readily cystallizes in contact with a crystal already formed.

C-Diethyloxacetylurea can also be obtained by boiling diethyloxyacetylcyanamide (see below) with dilute sulphuric acid (20 per cent), and shaking the ureide out with ether. After evaporation of the ether, a colorless oil remains, which on standing a short time solidifies to a colorless, crystalline mass, melting at 30°–31°.

0.3112 gram substance gave 0.6167 gram CO_2 and 0.2271 gram H_2O.

0.2312 gram substance gave 20.9 cc. N at 27° and 753 mm.

	Calculated for $C_{18}H_{24}N_2O_5$.	Found.
C	54.17	54.05
H	8.33	8.11
N	9.72	9.88

One hundred parts of water dissolve about 6.5 parts of the ureide at 20°, and about 14 parts at 100°. It is very easily soluble in alcohol, ether, chloroform, acetone, carbon disulphide, and benzene, only slightly soluble in warm, and nearly insoluble in cold petroleum ether. It dissolves in cold concentrated hydrochloric and sulphuric acid and separates out again unchanged on diluting with water.

By heating the salts in dry form a distillate was obtained which by repeated fractional distillation was separated into diethyl ketone, boiling at 101°–103°, diethylcarbinol, boiling at 116°–117°, and a compound which boiled at 140°–143°, probably triethylcarbinol.

According to its formula diethyloxyacetylurea should form two series of salts,

$$
\begin{array}{cc}
\begin{array}{l}
\text{C}_2\text{H}_5 \\
\hspace{1em}\diagdown \\
\hspace{1.5em}\text{C} \\
\hspace{1em}\diagup \hspace{1em}\diagdown \\
\text{C}_2\text{H}_5 \hspace{2em}\text{CO.NX} \\
\hspace{6em}\diagdown \\
\hspace{7em}\text{CO} \\
\hspace{6em}\diagup \\
\text{C}_2\text{H}_5 \hspace{2em}\text{CO.NH} \\
\hspace{1em}\diagup \hspace{1em}\diagup \\
\hspace{1.5em}\text{C} \\
\hspace{1em}\diagdown \\
\text{C}_2\text{H}_5 \hspace{2em}\text{OH}
\end{array}
& \text{and} \hspace{1em}
\begin{array}{l}
\text{C}_2\text{H}_5 \\
\hspace{1em}\diagdown \\
\hspace{1.5em}\text{C} \\
\hspace{1em}\diagup \hspace{1em}\diagdown \\
\text{C}_2\text{H}_5 \hspace{2em}\text{CO.NX} \\
\hspace{6em}\diagdown \\
\hspace{7em}\text{CO ;} \\
\hspace{6em}\diagup \\
\text{C}_2\text{H}_5 \hspace{2em}\text{CO.NX} \\
\hspace{1em}\diagup \hspace{1em}\diagup \\
\hspace{1.5em}\text{C} \\
\hspace{1em}\diagdown \\
\text{C}_2\text{H}_5 \hspace{2em}\text{OH}
\end{array}
\end{array}
$$
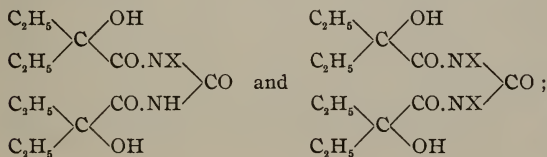
but only the normal seem to be capable of existence.

The normal alkali salts are prepared by treating the ureide with the equivalent amount of alkali hydroxide, or by boiling it with the equivalent amount of alkali carbonate and evaporating to dryness. They may be purified by dissolving them in ether-alcohol, filtering, evaporating to dryness, and finally washing with ether. They are then obtained as hygroscopic, saline masses very soluble in water and alcohol, readily soluble in ether-alcohol, and insoluble in ether. They dissolve readily in warm acetone, from which they crystallize on cooling, and are precipitated as sticky masses by addition of ether.

We did not succeed in obtaining the acid salts by using half the amount of alkali.

The *calcium salt*, $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_5\text{Ca}$, is best obtained by boiling the ureide with excess of lime, filtering, and evaporating the filtrate to dryness. It is freed from calcium oxide by

dissolving it in alcohol, and forms a hygroscopic, glassy mass very soluble in water and alcohol, insoluble in ether and acetone.

The *magnesium salt* is made in a similar way. White, non-hygroscopic powder, readily soluble in water, less so in alcohol. From its aqueous solution it is thrown down by acetone as a flocculent precipitate. For analysis it was dried at $100°$.

0.5360 gram substance gave 0.0695 gram MgO.

	Calculated for $C_{13}H_{22}N_2O_5Mg$.	Found.
Mg	7.85	7.79

When copper chloride is added to an excess of not too dilute solutions of calcium, barium, strontium, or magnesium salts of diethyloxyacetylurea, double salts of the formula $C_{26}H_{44}N_4O_{10}CuR$ are precipitated as light blue bodies, insoluble in water and alcohol. They are quite soluble in excess of copper chloride, but if these solutions are left standing, green precipitates of the normal copper salt are formed, and the same decomposition takes place by boiling the double salts with water. For analysis the magnesium copper salt was dried at $100°$.

0.3529 gram substance gave 0.0427 gram Cu_2S and 0.0592 gram $Mg_2P_2O_7$.

	Calculated for $C_{26}H_{44}N_4O_{10}CuMg$.	Found.
Cu	9.64	9.66
Mg	3.69	3.63

The *normal copper salt* is best obtained by adding a solution of the magnesium ureide to an excess of copper sulphate, and boiling the mixture, or by precipitating a solution of alkali ureide with copper sulphate. It forms a bluish green powder.

If copper sulphate is added to a solution of one molecule diethyloxyacetylurea in one molecule sodium hydroxide, a dark blue, sticky mass is precipitated, and the liquid assumes a dark blue color. Care must be taken not to add the copper sulphate in excess. The precipitate is washed with cold water and dissolved in alcohol. After evaporation

of the alcohol an ultramarine blue powder remains. It is only slightly soluble in water, quite readily in alcohol, easily soluble in chloroform with dark blue color, and nearly insoluble in ether. The content of copper corresponds with that of the acid salt, and by boiling with water it is changed to the normal salt described above. For analysis it was washed with ether and dried *in vacuo* over sulphuric acid.

0.5300 gram substance gave 0.0660 gram Cu_2S.

	Calculated for $C_{26}H_{46}N_4O_{10}Cu$.	Found.
Cu	9.98	9.94

The *zinc salt* is obtained by boiling the ureide with excess of zinc oxide, filtering, and concentrating the filtrate. It then separates out as small, glistening needles, nearly insoluble in cold water, slightly soluble in hot, and insoluble in alcohol. It contains two molecules water of crystallization, which it does not lose at 100°; the water, however, is given off at 130°, but at the same time the salt begins to decompose. For analysis it was washed with alcohol and dried at 100°.

0.3200 gram substance gave 0.0665 gram ZnO.

	Calculated for $C_{13}H_{22}N_2O_5Zn.2H_2O$.	Found.
Zn	16.88	16.70

The *silver salt* is precipitated as a white sticky mass by adding silver nitrate to a solution of the magnesium ureide. Recrystallized from hot water it forms shining, monoclinic prisms. On being heated with water it melts and then dissolves. It is quite readily soluble in hot water, less so in cold, and easily soluble in absolute alcohol, chloroform, and acetone, insoluble in ether. Dried in the air and *in vacuo* over sulphuric acid it still contains two molecules water of crystallization, from which it cannot be freed without decomposition. For analysis it was dried *in vacuo* over sulphuric acid.

0.3860 gram substance gave 0.1548 gram Ag.

	Calculated for $C_{12}H_{22}N_2O_5Ag_2\ 2H_2O$.	Found.
Ag	40.13	40.10

Mercury chloride precipitates the *mercury salt* as a white powder, nearly insoluble in cold and quite readily soluble in boiling water, from which it crystallizes in silky needles. It is readily soluble in alcohol and acetone and is precipitated from these solutions by addition of water; is easily soluble in chloroform, and insoluble in ether. Dried at 100° it retains one molecule water of crystallization.

0.3880 gram substance gave 0.1790 gram HgS.

	Calculated for $C_{13}H_{22}N_2O_5Hg.H_2O$.	Found.
Hg	39.68	39.86

C-Dipropyloxyacetylurea, $\dfrac{(C_3H_7)_2C.OH.CO.NH}{(C_3H_7)_2C.OH.CO.NH}{>}CO.$—This

compound was made in the same way as the diethylureide, by dissolving 5 grams sodium in 100 cc. absolute alcohol, adding to the cooled solution 37.6 grams ethyl dipropyloxyacetate and 7 grams urea, and boiling for some hours. The reaction product was slightly acidified with diluted hydrochloric acid, the alcohol distilled off, and the oily layer of dipropyloxyacetyl-urea separated from the salt solution, washed with water, dried, and distilled *in vacuo*. The main portion passed over at 188° under 25 mm. pressure, and after a second distillation boiled constantly at 186°–188° under 25 mm. pressure. The yield was 26 grams, which is about 76 per cent of the calculated.

0.3502 gram substance gave 0.7584 gram CO_2 and 0.2823 gram H_2O.

0.3077 gram substance gave 23.8 cc. N at 26° and 738 mm.

	Calculated for $C_{17}H_{32}N_2O_5$.	Found.
C	59.30	59.06
H	9.30	8.96
N	8.14	8.33

It forms a colorless, oily liquid, which by standing in the cold slowly solidifies to a white, crystalline mass. In contact with a fragment of the substance already crystallized, it solidifies instantly. On being heated it begins to soften at 35° and melts at 39°.

C-Dipropyloxyacetylurea may also be obtained by boiling dipropyloxyacetylcyanamide (see below) with diluted sulphuric acid (10 per cent), and shaking the ureide out with ether. After evaporation of the ether a colorless oil remains, which, without having been distilled, solidifies to a white crystalline mass on standing a short time in a cool place. Melting point‘ 39°.

0.3122 gram substance gave 0.6778 gram CO_2 and 0.2557 gram H_2O.

0.2132 gram substance gave 16.4 cc. N at 26° and 741 mm.

	Calculated for $C_{17}H_{32}N_2O_5$.	Found.
C	59.30	59.21
H	9.30	9.10
N	8.14	8.32

The ureide is only slightly soluble in cold water, more so in hot, easily soluble in alcohol, ether, acetone, chloroform, and benzene, difficultly soluble in petroleum ether. It acts as a dibasic acid.

The alkali salts are easily soluble in water, whereas the other salts are much less soluble than the corresponding salts of diethyloxyacetylurea.

The *magnesium salt* can be made by boiling the ureide with excess of magnesia, filtering, and evaporating the filtrate to dryness. It forms a white powder, only slightly soluble in cold water, more so in hot, and nearly insoluble in alcohol. For analysis it was washed with alcohol and dried at 100°.

0.5121 gram substance gave 0.0563 gram MgO.

	Calculated for $C_{17}H_{30}N_2O_5Mg$.	Found.
Mg	6.65	6.60

The *mercury salt* is precipitated by adding mercury chloride to a solution of alkali dipropyloxyacetylurea. It is nearly insoluble in cold water and dissolves in a large amount of boiling water, from which it separates out in microscopic needles.

The ethyl dipropyloxyacetate we used was obtained exactly in the same way as the ethyl diethyl ester, and although the

yield was not as good, it still was quite satisfactory.　Boiling point, 208°–210°.

C-Dimethyloxyacetylurea or α-Oxyisobutyrylurea,

$$(CH_3)_2CO.OH.CO.NH$$
$$(CH_3)_2CO.OH.CO.NH \big\rangle CO,$$ was made by dissolving 4.6 grams

sodium in 100 cc. absolute alcohol, adding 26.4 grams ethyl dimethyloxyacetate and 7 grams urea to the cooled solution, and boiling for some hours.　The reaction product was acidified, the alcohol distilled off, and the dimethyloxyacetylurea shaken out with ether.　After evaporating the ether it remained as an oily liquid, which, on cooling, solidified to a crystalline mass.　It is best purified by dissolving it in a large amount of boiling petroleum ether, from which it crystallizes in silky, snow white needles, or, on slow cooling, in glistening needles, often several cm. long.　It melts at 74°.　The yield was 21 grams, which is about 91 per cent of the theoretical.

0.1471 gram substance gave 0.2511 gram CO_2 and 0.0887 gram H_2O.

0.2002 gram substance gave 22.2 cc. N at 27° and 752 mm.

	Calculated for $C_9H_{16}N_2O_5$.	Found.
C	46.55	46.56
H	6.90	6.70
N	12.07	12.11

C-Dimethyloxyacetylurea can also be made by boiling dimethyloxyacetylcyanamide with diluted sulphuric acid, and shaking the ureide out with ether.　After evaporation of the ether, it remains as a colorless crystalline mass, which, when recrystallized from boiling petroleum ether, melts at 74°.

0.1735 gram substance gave 0.2952 gram CO_2 and 0.1049 gram H_2O.

0.2125 gram substance gave 23.8 cc. N at 28° and 752 mm.

	Calculated for $C_9H_{16}N_2O_5$.	Found.
C	46.55	46.40
H	6.90	6.72
N	12.07	12.16

Dimethyloxyacetylurea is readily soluble in both cold and hot water, easily soluble in alcohol, ether, acetone, chloroform, and benzene, only slightly soluble in warm, and nearly insoluble in cold petroleum ether.

The alkali and the alkali earth salts of this ureide are made in the same way as the corresponding salts of the diethyloxyacetylurea and resemble them very much.

The double salts $C_{18}H_{28}N_4O_{10}CuR$ (where R = Ca, Ba, Sr, or Mg) are precipitated in the usual way, as light blue substances, but only from quite strong solutions. The *normal zinc salt*, obtained by boiling the ureide with zinc oxide, filtering, and evaporating the filtrate to dryness, is easily soluble in both cold and hot water. It contains two molecules water of crystallization, which it does not lose at 100°.

For analysis it was washed with alcohol and dried at 100°. 0.2220 gram substance gave 0.0542 gram ZnO.

	Calculated for $C_9H_{14}N_2O_5Zn.2H_2O$.	Found.
Zn	19.73	19.62

The *normal silver salt* can be made by boiling the ureide with silver carbonate, or by precipitating a strong solution of alkali ureide with silver nitrate. Recrystallized from a little warm water, it forms small prisms, soluble in both cold and warm water.

Dried *in vacuo* over sulphuric acid it still contains one molecule water of crystallization.

0.3122 gram substance gave 0.1446 gram Ag.

	Calculated for $C_9H_{14}N_2O_5Ag_2.H_2O$.	Found.
Ag	46.54	46.32

The ethyl dimethyloxyacetate we used was made by heating potassium dimethyloxyacetate with ethyl iodide to 130,[1] and only the portion boiling exactly at 150° was employed. Concerning the preparation of dimethyloxyacetic acid we would like to mention that it has been our experience that most of the methods given in the literature are not well adapted for

[1] Fittig: Ann. Chem. (Liebig), **188**, 54.

making it in quantities, as either the yield is very low, or the processes tedious and expensive. The only process which gave us a satisfactory yield was Markownikow's.[1] A mixture of acetone, hydrocyanic acid, and diluted hydrochloric acid is left standing for 3 weeks, then boiled 3 days, the acetone distilled off, and the acid shaken out with ether.

C-Diethyloxyacetylthiourea,
$$\begin{matrix} (C_2H_5)_2C.OH.CO.NH \\ (C_2H_5)_2C.OH.CO.NH \end{matrix} \Big\rangle CS, \quad \text{was}$$
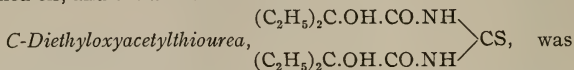
prepared as follows: 26.4 grams diethyloxyacetic acid were mixed with 10 grams thiourea and heated in an oil bath to 180° for several hours. The reaction product, which formed a thick, brownish oil, was washed with cold water, and then dissolved in a sufficient amount of boiling water. On letting the solution stand, diethyloxyacetylthiourea separated out, sometimes as crystals, but most frequently in the form of an oil. The mother liquor contained smaller or larger amounts of diethylthiohydantoin, which could be obtained by concentration of the liquid.

The diethyloxyacetylthiourea was again dissolved in a large amount of boiling water, and the solution allowed to stand, whereupon the substance crystallized out, either as long slender, yellow needles, or as small, rhombic prisms. By repeating the recrystallization, the substance was at last obtained colorless. It melted at 117°–118°, and this melting point was not changed by a further recrystallization. For analysis it was dried at 80°.

0.2173 gram substance gave 0.4066 gram CO_2 and 0.1500 gram H_2O.

0.3028 gram substance gave 25.0 cc. N at 23° and 745 mm.

0.1880 gram substance gave 0.1435 gram $BaSO_4$.

	Calculated for $C_{13}H_{24}N_2O_4S$.	Found.
C	51.31	51.03
H	7.89	7.67
N	9.21	9.12
S	10.54	10.50

[1] Ann. Chem. (Liebig), **146**, 339.

The yield was far from satisfactory, however, and in our various efforts to improve it, we did not meet with success.

The substance is only slightly soluble in hot water, insoluble in cold, and easily soluble in most organic solvents. It dissolves readily in alkalies and separates out again on the addition of acids. The substance begins to sublime below 100°. It is a very stable compound, and boiling with acids or alkalies does not seem to affect it.
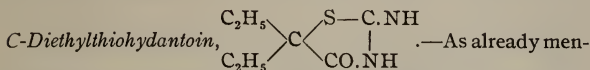
C-Diethylthiohydantoin, $\begin{array}{c} C_2H_5 \\ \diagdown \\ C_2H_5 \end{array} C \begin{array}{c} \diagup S-C.NH \\ | \\ \diagdown CO.NH \end{array}$.—As already mentioned, this compound is formed, together with the thioureide, when a mixture of diethyloxyacetic acid and thiourea is heated to 180°, but a better yield is obtained by raising the temperature to 200° and taking a large excess of thiourea. Accordingly 26.4 grams diethyloxyacetic acid were mixed with 20 grams thiourea and heated to 200° for five hours. The reaction product was washed with cold water, then treated with boiling water, filtered, and the filtrate concentrated. On letting the solution stand, the diethylthiohydantoin crystallized out, frequently mixed with diethyloxyacetylthiourea. These two substances were separated by treatment with ether, in which the thiohydantoin is only slightly soluble, whereas the thioureide is easily soluble. Recrystallized from boiling water it was obtained as colorless crystals, melting constant at 224°. The crystals belong to the regular system and consist mostly of cubes and octahedrons or a combination of these. For analysis the substance was dried at 100°.

0.1466 gram substance gave 0.2641 gram CO_2 and 0.0955 gram H_2O.

0.1311 gram substance gave 19.7 cc. N at 25° and 745 mm.
0.1040 gram substance gave 0.1420 gram $BaSO_4$.

	Calculated for $C_7H_{12}N_2OS$.	Found.
C	48.82	49.13
H	6.97	7.24
N	16.27	16.42
S	18.63	18.77

The substance is difficultly soluble in cold, readily so in hot water, easily soluble in alcohol and acetone, and very slightly soluble in ether. From chloroform it can be obtained as silky needles. It dissolves in alkalies and is precipitated from these solutions by addition of acids, but redissolves in excess of these.

By boiling with barium hydroxide the *C*-diethylthiohydantoin, as already mentioned, is converted into *C*-diethylthioglycolamide,
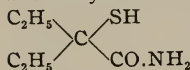
$$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} SH \\ CO.NH_2 \end{array}$$, and by continued boiling into diethyl-

thioglycollic acid, $$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} SH \\ COOH \end{array}$$. The operation was car-

ried out as follows: The thiohydantoin was boiled for one hour with an excess of baryta, and the cooled mixture slightly acidified with hydrochloric acid, whereupon an oil and a crystalline substance, both colorless, separated out. They were taken up with ether. After evaporation of the ether the crystals were separated from the oil as well as possible and recrystallized from boiling water. By repeating the recrystallization we finally obtained a substance melting constant at 147°. For analysis it was dried at 100°.
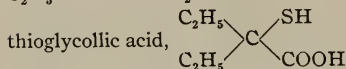
0.1103 gram substance gave 9.9 cc. N at 26° and 743 mm.
0.1078 gram substance gave 0.1721 gram $BaSO_4$.

	Calculated for $C_6H_{12}NOS$	Found.
N	9.52	9.73
S	21.80	21.95

Another portion of thiohydantoin, together with the oil formed in the above experiment, were boiled with baryta for 24 hours, and then made faintly acid with hydrochloric acid. The oil which separated out was shaken out with ether several times, the ether evaporated, and the remaining colorless oil dissolved in just enough boiling water. On cooling, the substance separated out as an oil. On standing *in vacuo* over sulphuric acid, the oil showed signs of crystallization, but as we have already stated, the examination of these two sub-

stances must be regarded as only preliminary on account of lack of material.

The substance did not contain nitrogen, which shows that the diethylthioglycolamide was completely converted into the acid.

0.1231 gram substance gave 0.1909 gram $BaSO_4$.

	Calculated for $C_6H_{12}O_2S$.	Found.
S	21.65	21.32

Dialkyloxyacetylcyanamides.

As already mentioned the dialkyloxyacetylcyanamides were obtained by a process which we expected would yield the thioureides and guaneides, namely, by heating a mixture of the esters of the dialkyloxyacetic acids and thiourea or guanidine with an alcoholic solution of sodium alcoholate. Instead of free guanidine, we employed guanidine sulphocyanide, as this is so easily obtained pure and dry.

Diethyloxyacetylcyanamide,
$$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!\!>\!\!C\!\!<\!\!\begin{array}{c} OH \\ CO.NH.CN \end{array}$$
, was made

as follows: 4.6 grams sodium were dissolved in 100 cc. absolute alcohol, and to the cooled solution were added 16 grams ethyl diethyloxyacetate and 8 grams thiourea. The mixture was boiled for several hours in a flask with reflux condenser, and then cooled. The reaction product was very carefully neutralized with diluted acetic acid, or better, the acid was added in slight excess, and then neutralized with a solution of sodium carbonate. Upon adding the acid a strong evolution of hydrogen sulphide took place, caused by the action of the acid on the sodium sulphhydrate formed during the reaction. After evaporation of the alcohol on the steam bath, the cyanamide separated out in shining plates, which, after being washed with ether, were recrystallized from boiling water. It then melted constant at 235°. The yield was 13 grams, which is about 83 per cent of the theoretical.

By using 12 grams guanidine sulphocyanide instead of the thiourea, but otherwise conducting the operation in exactly

the same way, an identical substance was obtained, but the yield was lower, namely, 11 grams, which is about 71 per cent of the theoretical. For analysis the substance was dried at 100°.

0.2037 gram substance gave 0.4014 gram CO_2 and 0.1441 gram H_2O.

0.1846 gram substance gave 30.9 cc. N at 29° and 747 mm.

	Calculated for $C_7H_{12}O_2N_2$,	Found.
C	53.85	53.74
H	7.69	7.86
N	17.95	17.94

Crystallized from water it forms colorless, glistening, monoclinic plates. It is only slightly soluble in cold, more so in hot water, and readily soluble in alcohol. It is very sparingly soluble in ether and chloroform, slightly more so in acetone, and practically insoluble in petroleum ether. It is easily soluble in cold diluted alkalies and is precipitated from these solutions by addition of acids, but redissolves in excess of these. On being heated carefully in a test tube, it melts, then volatilizes without decomposition, and condenses in the upper part of the test tube in the form of small crystals.

On boiling with moderately strong acids or alkalies it is quantitatively transformed into diethyloxyacetylurea, the following reaction taking place:

$$2\ \begin{array}{c}C_2H_5\\C_2H_5\end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c}OH\\CO.NH.CN\end{array} + 3H_2O =$$

$$\begin{array}{c}(C_2H_5)_2C.OH.CO.NH\\(C_2H_5)_2C.OH.CO.NH\end{array}\!\!>\!\!CO + 2NH_3 + CO_2.$$
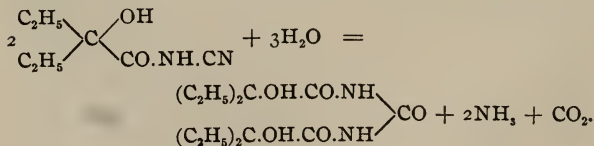
One gram substance was boiled for one hour with 50 cc. sulphuric acid (10 per cent) in a flask with reflux condenser. After cooling, the contents of the flask were carefully neutralized with sodium hydroxide, an excess of magnesia added, the ammonia distilled off, taken up in 0.5 N sulphuric acid, and the

excess of acid titrated with 0.5 N sodium hydroxide: 12.73 cc. acid were used.

The solution remaining in the flask was concentrated, acidified, shaken out with ether several times, the ether evaporated, and the diethyloxyacetylurea remaining dried *in vacuo* over sulphuric acid.

	Calculated for 1 gram diethyloxyacetylcyanamide.	Found.
NH_3	0.1090	0.1082
Diethyloxyacetylurea	0.9231	0.9105

This shows that the yields of ammonia and ureide are respectively 99.3 per cent and 98.6 per cent of the theoretical.

Dipropyloxyacetylcyanamide, $\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix} > C < \begin{matrix} OH \\ CO.NH.CN \end{matrix}$, was
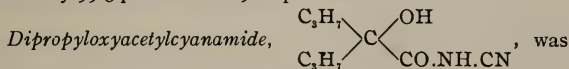
made in the same way as the diethyl compound. Four and six-tenths grams sodium were dissolved in 100 cc. absolute alcohol, and to the cooled solution were added 18.8 grams ethyl dipropyloxyacetate and 8 grams thiourea. The whole was boiled for several hours, then cooled, slightly acidified with diluted acetic acid, and the excess of acid carefully neutralized with sodium carbonate. After evaporation of the alcohol, the dipropyloxyacetylcyanamide crystallized out. It was washed with ether. Recrystallized from boiling water, it forms colorless, monoclinic needles, melting constant at 184°. The yield was 15 grams, which is about 82 per cent of the theoretical. By using 12 grams guanidine sulphocyanide instead of thiourea, the same substance was obtained, but the yield was lower. For analysis it was dried at 100°.

0.1831 gram substance gave 0.3939 gram CO_2 and 0.1431 gram H_2O.

0.1781 gram substance gave 24.8 cc. N at 27° and 758 mm.

	Calculated for $C_9H_{16}O_2N_2$.	Found.
C	58.70	58.67
H	8.70	8.68
N	15.22	15.33

Dipropyloxyacetylcyanamide is only sparingly soluble in cold water, more so in hot water, and easily soluble in alcohol.

In ether it dissolves but very slightly, more so in chloroform, and quite readily in acetone. Like the diethyl compound it dissolves easily in diluted alkalies, is precipitated from these solutions by acids, but redissolves in excess of these. On boiling with moderately strong acids or alkalies, it is quantitatively converted into dipropyloxyacetylurea.

Carefully heated above its melting point it volatilizes without decomposition and condenses in the form of small, silky needles.

Dimethyloxyacetylcyanamide or α-Oxyisobutyrylcyanamide,

$$\begin{matrix} CH_3 \\ \end{matrix} \begin{matrix} OH \\ C \\ \end{matrix} \begin{matrix} \\ \\ CO.NH.CN \end{matrix}$$

.—Four and six-tenths grams sodium were dissolved in 100 cc. absolute alcohol, and to the cooled solution were added 13.2 grams ethyl dimethyloxyacetate and 8 grams thiourea. The process was then carried on as usual, and the neutralized solution evaporated to a small volume, whereupon the dimethyloxyacetylcyanamide crystallized on cooling. It was washed with ether and dissolved in just sufficient boiling water, from which it crystallized in tiny, colorless, monoclinic needles, melting at 248°–250°. The yield was 9.5 grams, which is about 74 per cent of the theoretical. For analysis the substance was dried at 100°.

0.1507 gram substance gave 0.2586 gram CO_2 and 0.0857 gram H_2O.

0.2410 gram substance gave 48.2 cc. N at 27° and 750 mm.

	Calculated for $C_5H_8N_2O_2$.	Found.
C	46.88	46.80
H	6.25	6.32
N	21.88	21.77

The dimethyloxyacetylcyanamide is quite readily soluble in cold water, easily so in hot water and alcohol, and practically insoluble in ether, acetone, and petroleum ether. Heated carefully above its melting point it volatilizes and condenses again as small crystals. On boiling with moderately strong acids or alkalies, it is quantitatively converted into *C*-dimethyloxyacetylurea.

WATER OF CRYSTALLIZATION AS AFFECTED BY LIGHT (I).

By Ralph H. McKee and Elvin J. Berkheiser.

The study of this subject was occasioned by the fact noticed by one of us that of two portions of a preparation of p-aminobenzenesulphonic acid, commonly called sulphanilic acid, one portion which had been kept on a shelf and exposed to strong light had apparently lost much more of its water of crystallization than the other portion of the same preparation which had been kept in the dark.

An investigation of the literature failed to disclose any reference to the fact that light had been observed to have an effect on water of crystallization. The references to sulphanilic acid brought out the related facts, first, that the acid cannot be kept in its ordinary crystalline form but gradually "weathers" owing to a loss of water of crystallization and, second, that it can be obtained in a crystalline form free from water when fuming hydrochloric acid is used as the solvent.[1]

Some of the sulphanilic acid used was a "weathered" sample of König's make which had been on our shelves in a clear glass bottle for nearly ten years and had lost all but a trace of its water. The major portion was prepared by heating aniline with concentrated sulphuric acid according to Schmitt's method.[2] Titration of weighed amounts with tenth normal barium hydroxide and phenolphthalein gave excellent agreement with the values calculated from the formula

$$NH_2.C_6H_4.SO_3H.2H_2O.$$
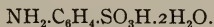
Samples of this hydrated acid were placed in two tubes, A and B. Tube B was like tube A except that it was wrapped in black lightproof paper. These tubes were loosely stoppered with absorbent cotton and exposed side by side to direct sunlight for ten winter days. Examination of the material in each tube by titration of weighed portions with standard barium hydroxide, and by heating at 100° to constant weight,

[1] Laar: Ber. d. chem. Ges., **14**, 1933 (1881).
[2] Ann. Chem. (Liebig), **120**, 132 (1861).

showed that the sample exposed to light had lost more than 98 per cent of its water of crystallization, while the sample wrapped in lightproof paper had lost but 35 per cent.

The temperatures of the samples were determined by two thermometers graduated to tenths of a degree and capable of easy estimation of the hundredths of a degree. A comparison of the two showed that they agreed within the error of reading (0°.01). They were inserted into the tubes until the bulbs were entirely surrounded by the crystals and, as in all the experiments, the tubes were closed with absorbent cotton. For complete certainty, after the temperatures had been once read, the thermometers were interchanged and temperatures read again. Determinations of the temperatures by this method showed that in direct sunlight the thermometer in the tube wrapped in black paper read 30°.42 while in the unwrapped tube was 2°.86 lower. In diffused light the temperature of the crystals in the wrapped tube was 20°.46 and in the unwrapped tube 1°.36 lower. In other words, the material at the lower temperature, but in the light, lost water faster than the one at the higher temperature, but in the dark.

The possibility that light had produced some change other than simply that of increasing the speed with which the water was given up by the crystals, such as a transformation into the ortho or meta acid, was considered and tested in the following ways:

1. Parallel determinations of the solubility in water of samples which had lost their water of crystallization by heat, and by light, gave results which agreed and were much below what would be expected for the ortho[1] and meta[2] acids. It may be added that the solubility of the anhydrous acid is about 3.5 per cent less than that of the hydrated form, determined simultaneously.[3]

2. Some of the acid which had been exposed to the light was dissolved in dilute sodium hydroxide and precipitated by adding

[1] Thomas: Ann. Chem. (Liebig), **186**, 128 (1877); and Bahlmann: *Ibid.*, **186**, 309 (1877).

[2] Berndsen: *Ibid.*, **177**, 83 (1875).

[3] For the solubilities of the hydrated form of the *p*-aminobenzenesulphonic acid compare Dolinski: Ber. d. chem. Ges., **38**, 1836 (1905).

concentrated hydrochloric acid. After drying at room temperature titration of weighed portions with standard alkali showed that by this recrystallization it had recovered its two molecules of water. The o-aminobenzenesulphonic acid crystallizes with 0.5 molecule of water of crystallization and the meta ordinarily water-free, though if a low temperature is used and special care taken it may be obtained with 1.5 molecules of water.

3. When some of the acid which had been exposed to light was recrystallized from warm water and care taken to have the solution so dilute that the separation of crystals did not occur until the temperature had fallen to 40° the crystals obtained had again their two molecules of water.

It was also shown that when sulphanilic acid which either contains its full amount of water or has lost its water by exposure to light was crystallized from water above 80° the crystals obtained were almost entirely free from water.

The fact that light affects water of crystallization is additional evidence to that accumulating in other quarters that such water is in real chemical combination and that we should consider the compound $NH_2.C_6H_4.SO_3H.2H_2O$, for example, as a single molecule instead of one molecule of aminobenzenesulphonic acid and two molecules of water. From this point of view the term "hydrate" to designate a substance with water of crystallization has much in its favor, for in the short term there is little suggestion of the existence in the crystalline substance of water molecules as such.[1]

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THE BASICITY OF ACIDS AS DETERMINED BY THEIR CONDUCTIVITIES.

BY M. R. SCHMIDT.

In his work on organic acids,[2] D. Berthelot showed that when an acid is treated with increasing amounts of alkali, its

[1] The investigation is being continued with other substances. The effect of light of various colors is also being studied.—RALPH H. McKEE.

[2] Ann. Chim. Phys. [6], **23**, and **24** (1891).

conductivity decreases to a minimum, which is reached when sufficient base has been added to neutralize the acid. Further addition of alkali causes the conductivity to increase. This is what would be expected. The swiftly moving hydrogen ions are removed from the sphere of conductivity, owing to the formation of water, and the smaller velocity of the metal ions causes the decrease in conductivity. When, however, an excess of base is added, the presence of a greater number of metal and, especially of hydroxyl ions, causes the conductivity to increase again. This is simply another expression of the fact that the conductivity of a salt is, generally speaking, less than that of its component acid or base.

If this method is applied to polybasic acids, a minimum is found when enough alkali has been added to form the primary salt. Then the conductivity rises and continues to rise even after the secondary salt has been formed, but with a different rate of increase. If the conductivities are plotted as ordinates and the amounts of alkali added as abscissas, a sharp minimum is found at the point corresponding to the primary salt when the dilution is great. The curve then rises to the point denoting the secondary salt, but from here to the point corresponding to the formation of the tertiary salt, a *change of slope* is noticed, and so on. Berthelot[1] employed this method of partial neutralization in the study of phosphoric acid, and came to the conclusion that phosphoric acid is not a true tribasic acid, but a monobasic acid " of complex function," in which the first hydrogen to be replaced by metals resembles the characteristic ion of strong acids, the second the slightly dissociated hydrogen of weak acids, and the third the hydrogen of the hydroxyl group in phenols, etc.

Miolati and Mascetti,[2] using a modification of Berthelot's method, studied the effect of alkalies on the conductivities of solutions of sulphurous, selenous, selenic, telluric, arsenious, arsenic, phosphorus, boric, chromic, iodic and periodic acids. In every case a minimum conductivity was found when suffi-

[1] Ann. Chim. Phys. [6], **38**, 1 (1893).
[2] Gazz. Chim. Ital. **31** [1], 93 (1901).

cient alkali had been added to neutralize one hydrogen, and a marked change in slope was noticed in the curves when the second hydrogen was replaced by metals.

In a recent article,[1] Pellini and Pegararo have shown that the same method, applied to hydrofluoric acid, leads to the interesting conclusion that this substance, in solution, behaves as a dibasic acid. Evidence on this point from other sources is conflicting. On the one hand, the existence of such well-known salts as KHF_2 and $RbHF_2$ seems to lend support to the view that hydrofluoric acid is dibasic. Peratoner and Paterno[2] made some cryoscopic measurements which they interpreted as furnishing evidence for the dibasic character of hydrofluoric acid. They obtained a molecular lowering of the freezing point of about $2°.0$, as against $3°.6$ for hydrochloric acid; and concluded that hydrofluoric acid should have, in aqueous solution, the formula H_2F_2. But, in the light of the theory of electrolytic dissociation, as Pellini and Pegararo point out, the results show rather that hydrofluoric acid exists in solution as the single molecules, which are only slightly dissociated. Moreover, the application to sodium fluoride and potassium fluoride of Ostwald's rule for determining the basicity of an acid, gives results which indicate that we are dealing with salts of a monobasic acid:

	$v.$	$\mu_{25°}.$	
NaF	1024	104.0	$\Delta = 11.0$
	32	93.0	
KF	1024	126.1	$\Delta = 11.4$
	32	114.7	

If sodium fluoride and potassium fluoride were salts of a dibasic acid, the value of Δ should be about 20.

In its conductivity, as compared with the other halogen acids, hydrofluoric acid shows a further peculiarity. The following figures, taken from Ostwald, indicate, as Pellini and Pegararo state, a wide variation from the behavior of the

[1] Gazz. Chim. Ital. **38** [1], 1 (1908); summarized in Z. Elek. Chem. **13**, 621 (1907).
[2] Rend. Acc. Linc. [4], **6**, 306 (1890).

ordinary halogen acids, on the one hand, and from that of the dibasic acids on the other.

V.	HF. $\mu_{25°}$.	HCl. $\mu_{25°}$.	HBr. $\mu_{25°}$.	HI. $\mu_{25°}$.
4	29.6	366	377	376
32	59.5	393	398	397
1024	224.0	. . .	405	404

Further illustration of the abnormal character of hydrofluoric acid is shown in the solubility of some of its salts. Silver fluoride, for instance, is easily soluble in water, while silver chloride, bromide and iodide are insoluble. Again, calcium chloride, bromide and iodide are deliquescent, while calcium fluoride is insoluble.

Pellini and Pegararo undertook to settle the question of the basicity of hydrofluoric acid by means of the method of neutralization here described. They worked at 25° and at a dilution of $V = 173$. Reckoning hydrofluoric acid as a monobasic acid, the minimum of conductivity was found when an amount of alkali had been added equivalent to one-half molecule of hydrofluoric acid. This result is in accord with all work previously done on acids known to be dibasic, such as sulphuric, chromic, telluric, etc. Moreover, there is a sudden change in the slope of the conductivity curve when complete neutralization is effected, as would be expected with a dibasic acid. The application of this same general method by Düllberg[1] to a number of acids, including dilute solutions of phosphoric acid, should also be mentioned.

Berthelot's work on phosphoric acid was carried out with solutions of moderate dilution. Work was taken up in this laboratory in order to ascertain the *behavior of phosphoric acid in fairly concentrated solutions*. For this purpose solutions were made up to contain 1, 0.5, 0.2, 0.1 gram molecules (98.03 grams) phosphoric acid in 1000 cc. The N solution was standardized against caustic potash and then checked by gravimetric determinations. The error in the strength of the solutions was probably ±0.3 per cent. In preparing

[1] Z. physik. Chem., **45**, 129 (1903).

the solutions for conductivity measurements, a plan differing slightly from that adopted by Berthelot, and Miolati and Mascetti was employed. Ten cc. of a phosphoric acid solution were taken, and to this was added one, two, three, etc., cc. caustic potash of the same molecular concentration. The volume of the whole was then brought to 50 cc. at 20°. Thus the solutions of the partially nuetralized phosphoric acid were 0.2, 0.1, 0.04 or 0.02 N with respect to PO_4. Consequently, the conductivities obtained are strictly comparable with other conductivity values, which is not the case with the results of the investigations above named. The values given in the table are equal to $s \times V$, where s is the specific conductivity of the solution; and, of course, in two cases, where the solutions contain only phosphoric acid or only primary potassium phosphate, $s \times V$ becomes equal to μ_v.

The standard of conductivity was that of a 0.02 N solution of potassium chloride at 25°, $\mu_v = 129.7$. All readings were made at 25°, and the conductivities are corrected for the water used.

An attempt was made to obtain measurements for a N solution of phosphoric acid, but, owing to the very small resistances that had to be used, accurate results were not possible.

cc. KOH added.	0.2 N H_3PO_4. $s \times V$.	0.1 N H_3PO_4. $s \times V$.	0.04 N H_3PO_4. $s \times V$.	0.02 N H_3PO_4. $s \times V$.
0	77.8	97.6	134.4	168.8
1	68.0	85.8	121.5	154.8
2	(57.2)	80.1	109.3	142.6
3	58.6	75.3	104.6	131.8
4	58.4	72.2	97.5	121.5
5	59.1	71.4	93.0	114.4
6	60.6	71.5	89.5	106.9
7	63.6	72.2	86.0	101.4
8	67.0	74.3	85.6	95.9
9	70.3	76.9	85.5	92.2
10	75.2	80.1	87.6	90.9
11	....	....	.....	101.9
12	....	....	.....	112.2
13	....	....	.....	122.8

The results are plotted in the accompanying figure.

Molecules KOH to one molecule H_3PO_4.
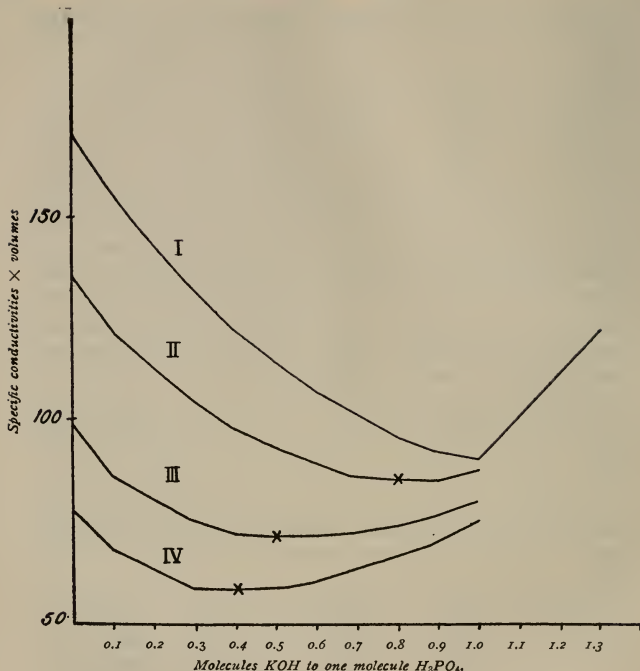
It will be noticed that only in one case—in the 0.02 N solutions curve I.—does the minimum fall at the point corresponding to the complete neutralization of one hydrogen. In the 0.2 N solutions (curve IV.) the minimum occurs when only about 40 per cent of the amount of the caustic potash required for one-third neutralization has been added. In the more dilute solutions, the minimum shifts continually towards the point corresponding to the salt, KH_2PO_4, reaches it in the 0.02 N curve (curve I.) and then remains stationary, as a trial with 0.01 N phosphoric acid proved.

The cause of this phenomenon has been suggested by Dr.

B. B. Turner. As more and more caustic potash is added, the $\overset{+}{H}$ ions of the phosphoric acid are replaced by $\overset{+}{K}$ ions, which move more slowly, and as a result the conductivity of the mixture decreases. But in a concentrated solution, phosphoric acid is far from completely dissociated. Hence, when a comparatively small amount of base has been added, practically all of the hydrogen ions present are neutralized but more immediately dissociate, and in sufficient quantity to overbalance the decrease in conductivity caused by the substitution of the $\overset{+}{K}$ ions for the $\overset{+}{H}$ ions. Therefore, the conductivity rises again, and a minimum appears before enough alkali has been added to form the primary salt. Furthermore, as the dilution of the phosphoric acid increases, the number of hydrogen ions present becomes greater, and continually increasing amounts of base are necessary to neutralize them. Consequently, a continually decreasing amount of hydrogen remains to dissociate from the H_3PO_4 molecule, and thus the minimum is found at points which continually approach the point corresponding to the salt KH_2PO_4. After a dilution of 0.02 N is reached, the phosphoric acid is dissociated according to the formulation

$$H_3PO_4 \rightleftarrows \overset{+}{H} + H_2\overset{-}{PO_4}$$
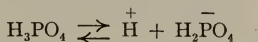
to such an extent that the increase in conductivity due to the dissociation of the hydrogen, after the $\overset{+}{H}$ ions already present have been neutralized, is not great enough to make up for the decrease in conductivity, and therefore the curve does not rise again until after the complete neutralization of the first hydrogen.

A method is here indicated by which the conductivity of any of the mixtures may be calculated. On the assumption that in the solutions worked with the second and third hydrogen ions of the acid are formed to only a negligible extent, we have, at the point of equilibrium, the following conditions: The primary potassium salt present in any mixture tends to drive back the dissociation of the phosphoric

acid, and the latter, in turn, tends to suppress the ionization of the salt KH_2PO_4. Hence, if no hydrolysis takes place, we may represent equilibrium by the formula

$$\overset{+}{H} + KH_2PO_4 \rightleftarrows \overset{+}{K} + H_3PO_4.$$
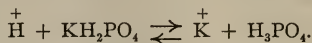
Let the total concentration of phosphoric acid, *i. e.*, of all ions or molecules containing the PO_4 group be represented by a; the total concentration of potassium by b; the undissociated phosphoric acid by x; and the undissociated primary potassium salt by y.

Now, the PO_4 group is present as

$$[H_3PO_4] + [H_2\overline{PO_4}] + [KH_2PO_4],$$

or

$$a = x + [H_2\overline{PO_4}] + y,$$

and

$$[H_2\overline{PO_4}] = a - x - y.$$

Also,

$$a = x + b + [\overset{+}{H}],$$

and

$$[\overset{+}{H}] = a - x - b,$$

and

$$[\overset{+}{K}] = b - y.$$

Hence, if the mass law holds, we have

$$\frac{(a - b - x)(a - x - y)}{x} = K$$

and

$$\frac{(b - y)(a - x - y)}{y} = K'.$$

K and K' are known, being the ionization constants of phosphoric acid and of primary potassium phosphate, respectively; also, a and b are known for any given mixture. From these values x and y can be calculated, and, since the relative velocities of the ions are known, we can calculate the

conductivity of each mixture of phosphoric acid and potassium phosphate.

In conclusion, I would express my thanks to Professor H. C. Jones, who suggested this investigation, and under whose guidance it was carried out.

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BALTIMORE, April, 1908.

REVIEWS.

MODERN PIGMENTS AND THEIR VEHICLES, THEIR PROPERTIES AND USES CONSIDERED MAINLY FROM THE PRACTICAL SIDE, AND HOW TO MAKE TINTS FROM THEM. By FREDERICK MAIRE, ex-Editor of "Painting and Decorating," author of the "Modern Wood Finisher," the "Modern Grainer." New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1908. Price, $2.

This book is written by a practical painter, who shows a very thorough knowledge of the materials of his craft. The subject matter includes a detailed description of all pigments used by painters and decorators, with method of manufacture or preparation, physical characteristics, uses and method of application of each. The pigments are divided in groups, based on color, with clear concise statements of the color, tone, tinting power, and general character of each. The chapters on "Compounding of Pigments" and "Test of Principal Tints and Pigments Required to Make Them" will be of much value to the practical painter, and will aid the chemist in the analysis of mixed paints. The table of synonyms is very complete and will be useful until some uniform system of nomenclature is adopted by the paint trade. The chapters on vehicles are rather unsatisfactory and incomplete. No mention is made of China-wood oil or wood turpentine. The chemistry of this subject is weak, as, in fact is the case all through the book. It is unfortunate that misstatements regarding formulae of white lead, red lead, the chemistry of the fixed oils, and theory of drying were not more carefully edited before the book was published. Altogether the volume will be of value to the progressive practical painter, but will be of but limited assistance to the chemist. S. S. VOORHEES.

DETECTION OF COMMON FOOD ADULTERANTS. By EDWIN M. BRUCE, Instructor in Chemistry, Indiana State Normal School. New York: The D. Van Nostrand Company. 1907. pp. 184. Price, $1.25, net.

The book is a compilation of qualitative tests for the detection of food adulterants. It is of value in interesting stu-

dents in the subject, but it is difficult to see what class of people can advantageously use a book, many of whose methods require so much care, experience, and skill and which yet is practically free from quantitative methods. Mohler's method for the determination of benzoic acid on page 10, for instance, requires more experience in its manipulation than is to be expected of one who is not proficient in quantitative as well as qualitative analysis. After the method is described comforting information is given that "If this test is not carefully performed, it is worthless, as other substances give similar results." This is followed by a paragraph directing the concentration of the alkaline solution and precipitation of the benzoic acid by acidifying. The same reaction is also given by other substances, but the author does not state that fact.

On page 8 the statement is made that one may test for nitrates by identifying the metal by a qualitative test for potassium.

The statement of the author on page 16 that alum may be added by millers to cover up bad flour is probably not true at the present time; that stannous chloride and potassium carbonate are added to ginger cake to influence color is also probably erroneous.

The book includes the old phenol and sulphuric acid test for formaldehyde which was used before the modern methods were known, but which has long since been discarded.

The statement that gelatin may be added to increase the weight or thicken the more voluble adulterants of honey is also open to question.

On pages 60 and 63, the author says that lard from hogs fed on any of the various cottonseed products may give a faint reaction by Halphen's test. This would lead the unitiated to suppose that a strong reaction would not result from feeding hogs on cottonseed meal which repeated experiments have shown to be untrue.   W. D. BIGELOW.

STOICHIOMETRY. By SIDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in the University of Dublin. With Eighty-eight Figures in the Text. Together with an Introduction to the Study of Physical Chemistry by SIR WILLIAM RAMSAY, K.C.B., F.R.S. 39 Paternoster Row, London; New York; Bombay and Calcutta: Longmans, Green and Co. 1908. pp. 381. Price, $2.

The contents of this admirable volume will show its scope: Fundamental Laws of Chemical Combination, General Properties of Gases, Determination of Atomic Weights, The Periodic Law, The Dissociation of Gases and Vapors, The Prop-

erties of Liquids, The Kinetic Theory of Gases, Properties of Solids, Mixtures, Solubility and Miscibility, Properties of Dilute Solutions, Dissolution and Vaporization, and the Determination of Molecular Weights.

The Introduction to the Study of Physical Chemistry published by Ramsay in Findlay's volume on the Phase Rule is repeated here, with a few additional pages at the end.

The book is very well written, as we would expect from the fact that it comes from the pen of Sidney Young, and is well worthy of the series of which it forms a part. There are, however, a few matters which we could wish were otherwise. On the first page of the text we find a paragraph on "The Conservation of Matter." This would be pretty bad, if the text did not explain so carefully and clearly what was meant. There is, of course, no such law known to man. We have absolutely no means of measuring matter, and even if it exists, do not know whether it is conserved in chemical reaction. What is meant is, of course, the law of the conservation of mass. The discussion of valency (pp. 100 to 104) is unsatisfactory. The subject is well illustrated and this is about all. That valency is a purely electrical phenomenon, governed by Faraday's law, which is its physical basis, is not made clear. Indeed, there are few subjects in any branch of science so unsatisfactorily discussed in general as chemical valence, and this is due primarily to a lack of any definite basis on which to begin the discussion. If we place valence upon a perfectly definite rigid physical basis—Faraday's Law—where it belongs, the discussion of this subject in a scientific manner would at least be made possible.

Another defect in the book is the clumsy appearance of the curve-sheets. The use of the double-lined ordinates, and the very heavy type inside and outside of the curve sheet proper, does not give a neat appearance.

These are, however, minor defects which can easily be corrected in a new edition.   H. C. J.

THERMOCHEMISTRY. By JULIUS THOMSEN, Emeritus Professor of Chemistry in the University of Copenhagen. Translated from the Danish by KATHARINE A. BURKE, B.Sc. (Lond.), Assistant in the Department of Chemistry, University College, London. 39 Pâternoster Row. London; New York; Bombay and Calcutta: Longmans, Green and Co. 1908. pp. 495. Price, $2.50.

It is fortunate that these classical investigations of Thomsen have been made a part of the Ramsay series of Text-books of Physical Chemistry, and this leads us to raise the question, What is the object of thermochemical measurements?

It is well known that we have no means of measuring directly the amount of intrinsic energy contained in elements or compounds. Since all chemical reactions are caused by a difference in the potential or the quantity of intrinsic energy present in the reacting substances, it is of the utmost importance for the science of chemistry that we should have some method of measuring at least the difference between the intrinsic energy of the substances before they react, and of the compounds formed.

When two substances are brought together which can react chemically, a part of their intrinsic energy is transformed, in a positive or negative sense, into heat. There is always a thermal change whenever any chemical reaction takes place. The amount of heat set free in a positive or negative sense is a measure of the energy change which takes place and which is the cause of the rearrangement of the system or systems into new systems which are stable for the new conditions; it is the cause of all chemical reactions.

We measure the heat of reactions, then, in order to learn the magnitude of the energy change. This assumes, of course, that there is no electrical energy and no light energy produced during the reaction and that no appreciable work done as is usually true.

Thermochemical measurements center around two laboratories, that of Berthelot, in Paris, and that of Julius Thomsen, in Copenhagen. The results obtained by Thomsen are, taken as a whole, certainly the most reliable that we have in this field, although it was Berthelot who reached the most important generalizations in this field.

We are fortunate in having thermochemical results brought together by one of the two great masters in this field, and brought together in such a convenient and accessible form. The larger divisions of the book are: Formation and Properties of Aqueous Solutions; Compounds of Nonmetals; Compounds of Metals with Nonmetals and Organic Substances.

The book is written in a very readable style, and we can, therefore, assume that the translation has been well done.

<div align="right">H. C. J.</div>

DAS LACHGAS. Eine chemisch-kulturhistorische Studie. Von Dr. ERNST COHEN. Mit 31 Autotypen im Text und einer farbigen Karikatur. Leipzig: Engelmann. 1907. pp. 99. Preis, M. 3.60.

A few years ago one of Gillray's caricatures, which is reproduced in the frontispiece of this pamphlet, came into the hands of the author. He has since spent a good deal of time in trying to determine its significance. As a result

of his researches he has learned much that is interesting regarding the "histoire intime" of laughing gas and now presents his results to the chemical public. The caricature is amusing though vulgar. To quote from a description published in 1802: "Most of the figures are portraits of the members of the (Royal) Institution. The gentleman experimented upon is Sir J. C. Hippesley; the operator, Dr. Garnet. The bellows are held by Sir Humphrey Davy, not then a baronet. To the extreme right (to the left of Davy) Count Rumford is easily recognized." Careful inquiry has revealed the fact that "the operator" depicted is not Dr. Garnet, but Dr. Thomas Young. The picture is intended as a burlesque on the Royal Institution.

It is interesting to note that the speculations of Samuel Latham Mitchill, professor of Natural History, Chemistry, and Agriculture in Columbia College, New York, had something to do with directing the attention of Davy to the study of the dephlogisticated nitrous gas (laughing gas) of Priestley. In 1796, Mitchill wrote to Rev. Dr. Henry Mehlenberg (Mühlenberg) in Lancaster, Pa., a letter "On septon (azote) and its compounds, as they operate on plants as food and on animals as poison." According to Mitchill's septon theory "dephlogisticated nitrous gas" or "oxide of septon" (nitrous oxide) is the cause of all infectious diseases. This letter came into Davy's hands and set him to work on nitrous oxide.

Mitchill was a very remarkable man. The universality of his knowledge is thus described: "He was now engaged with the anatomy of the egg, and now deciphering a Babylonian brick; now involved in the nature of meteoric stones; now in the different species of brassica; now in the vaporization of fresh water; now in that of salt; now scrutinizing the geology of Niagara; now anatomizing the tortoise; now offering suggestions to Garnet, of New Jersey, the correspondent of Mark-Akeuside, on the angle of the windmill; and now concurring with Michaux on the beauty of the black walnut as ornamental for parlor furniture; now with his cinchological friend, Samuel Akerly, in the investigation of bivalves; and now with the learned Jewish rabbi, Gershom Seixas, in exigetical disquisitions on Kennicott's Hebrew Bible. Now he might be waited upon by the indigent philosopher, Christopher Colles, to countenance his measures for the introduction of Bronx river into the city; and now a committee of soap boilers might seek after him to defend the innoxious influence of their vocation in a crowded population. For his services in this cause of the chandlers, Chancellor Livingston assured

him, doubtless facetiously, by letter, that he deserved a monument of hard soap.... In the morning he might be found composing songs for the nursery; at noon dietetically experimenting and writing on fishes, or unfolding to admiration a new theory on terrene formations; and at evening addressing his fair readers on the healthful influence of the alkalies and the depurative virtues of white washing."

Dr. Cohen's pamphlet is very interesting reading and from the historical point of view there is much that is valuable contained in it.   I. R.

AMERICAN

CHEMICAL JOURNAL

ELECTRIC OSMOSE.

[PRELIMINARY COMMUNICATION.]

BY J. C. W. FRAZER AND H. N. HOLMES.

In a series of experiments, made to determine the solution most efficient for removing the air from the pores of osmotic cells previous to the deposition of the semipermeable membrane,[1] the amount of water carried through the wall of the cell during the passage of a given current did not appear to be proportional to the resistance of the solutions of those electrolytes investigated, as deduced by Helmholtz.[2] The experiments given below were made to determine more accurately the relative osmose of a few of the salts of nitric acid at a concentration of 0.001 normal. Though the number of measurements is small and they are not as accurate as we hoped to get, it is thought best to publish the results now and continue the work at some future time.

Before presenting the results of the work a brief description will be given of the apparatus used. This is shown in the accompanying drawing.

The glass vessel B was made by cutting off the bottom of a half-liter bottle and inverting it as shown. The bottom

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[1] THIS JOURNAL, **26**, 80.
[2] Wied. Ann., **7**, 351 (1879).

of the bottle is used as a cover to protect the solution and the apparatus enclosed within. To secure a better joint between the two, a wide rubber band is slipped around the line of contact between the two parts of the bottle.
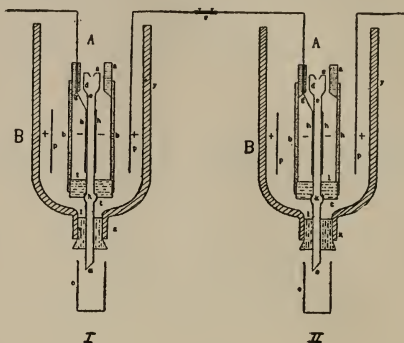
The porous clay cell b is ground round for a distance of 15 mm. at each end and the soapstone washers, a and i, turned to fit accurately into these ground ends. In the center of i is a hole just large enough to allow the entrance of the drainage tube e. This tube is enlarged at k and the bulb so formed set firmly with shellac in the cavity t, after which the whole connection is painted with a solution of rubber in carbon bisulphide. Before setting the washers, a and i, in place their surfaces and the ground portions of the porous cell are painted with some of the same solution and when the rubber has been thoroughly hardened the joints at the two ends of the cell are perfectly tight and rigid. The purpose of the washer a and the enlarged upper end d of the glass tube is to limit the amount of liquid in the upper part of the cell and to give a large surface over which the liquid draining from the cell may flow, without diminishing the contents of the cell. To secure proper draining of the liquid from the cell at d, platinum discs with serrated edges were ground on the lathe the exact diameter of d and the interior of these

caps was cut in the shape of teeth, meeting in the center, which are bent down so as to center the cap on d.

The platinum cathode h tightly clasps the glass tube and the wire leading to it passes through g. This hole is closed by the solution of rubber in carbon bisulphide. The anode p is a large platinum cylinder surrounding b.

The lower end of the glass tube e is ground to a sharp angle to facilitate the dropping of the liquid into the weighing bottle o.

The two parts, I. and II., of this apparatus are made as nearly alike as possible and are connected in series as shown in the illustration. The bottles rest upon a platform provided with two holes just large enough to admit their necks. This platform is simply a shelf in a box, so placed that the upper portions of the bottles project slightly through holes in the top of the box which is closed in front by a glass door, intended to exclude dust from the interior.

As jarring has considerable influence on the outflow of liquid at d the box is placed on an iron slab which is supported in sawdust.

To determine the point to which B must be filled previous to a measurement, it was filled with water to a point somewhat higher than c and allowed to stand for a long time until liquid ceased to drop from m, when a mark was made on B at the surface of the liquid. In operation B is filled to this mark and b to overflowing. After two minutes the weighing bottles are placed under m and a current of 36 volts passed for one minute through the two parts in series. After two minutes the overflow from each of the cells is weighed.

The object of having the apparatus duplicated is to use one of the parts, I., as a standard, keeping it always filled with 0.001 normal potassium nitrate solution so that the osmose of the solution in II. is expressed in terms of the osmose of that in I. Although the two parts, I. and II., were made as nearly alike as possible it is found ordinarily that when both are filled with the same solution different amounts of liquid will flow from the two. When both cells are filled with 0.001 normal solution of potassium nitrate the ratio of the amounts

of liquid escaping from I. and II. enables one to correct for
the differences in the two parts when some other electrolyte
is put into II., thus allowing all measurements made in II.
to be expressed in terms of the osmose of 0.001 normal potas-
sium nitrate in I. It has been found that this cell ratio changes
considerably when the apparatus is used too frequently or
when the current is kept on for any length of time, due, prob-
ably, to the cell wall becoming electrified. For this reason
the apparatus was not used frequently and the current kept
on only one minute, and the cell ratio, with 0.001 normal
potassium nitrate in both, was frequently redetermined.

The following tables give the relative osmose of the various
electrolytes indicated to that of potassium nitrate which
is assumed arbitrarily to be 100. All the solutions were
made 0.001 normal and the water which was used
had a conductivity of about 1.5×10^{-6} at $25°$.

Table I.—Sodium Nitrate.[1]

147.9	147.2	150.5	148.8
147.2	142.7	151.8	150.7
148.4	148.8	. . .	149.1

| Mean, | 147.8 | 146.2 | 151.1 | 149.5 |

Table II.—Ammonium Nitrate.

103.5	103.2	102.7
102.9	102.5	103.0
103.7	102.3	102.7

| Mean, | 103.4 | 102.6 | 102.8 |

Table III.—Lithium Nitrate.   Table IV.—Caesium Nitrate.

184.3	97.6
182.8	96.9
183.7	95.3
179.5	. .

| Mean, | 182.6 | | Mean, | 96.6 |

[1] These measurements of 0.001 sodium nitrate were made in an apparatus of
different form which has not been shown to be as reliable as the one described above,
but the results agree better among themselves.

Table V.—*Rubidium Nitrate.*

97.0	97.4	97.4	96.9
96.8	97.2	98.2	95.7

Mean, 97.1

Table VI.—*Barium Nitrate.*	Table VII.—*Calcium Nitrate.*
61.7	62.4
59.6	63.6
53.9	67.8
..	65.4
Mean, 58.4	Mean, 64.8

Table VIII.—*Strontium Nitrate.*

61.1
58.0
65.0

Mean, 61.3

Lack of time prevented a quantitative study of the osmose of acids and bases in a manner similar to the above work on the nitrates. But when cell I. was filled with 0.001 normal solution of potassium nitrate and cell II. with 0.001 normal nitric acid and the determination made just as had been done in one of the experiments given above it was found that the surface of the liquid inside the cell *b* fell. A second determination was made of nitric acid and the electrodes in part II. reversed. Liquid now dropped from both outlet tubes. In this and a number of similar experiments the amount of negative osmose from cell II. was about 14 per cent of that from cell I. Acetic acid (0.001 normal) was next put into cell II. and the negative osmose was much greater. The amount of liquid coming from cell II. was 1.28 times greater than that from cell I.

In the table below we have brought together the means of all the measurements made, together with the relative specific resistances of the solutions used. The values for the resistance are taken from Kohlrausch and Holborn's

"Leitvermögen der Elektrolyte" and for the sake of comparison are so calculated as to make the resistance of 0.001 normal potassium nitrate solution equal to 100, as shown in column IV.

I.	II.	III.	IV.
	Osmose.	Calculated osmose.	Relative specific resistance.
KNO$_3$	100.0	100.0	100.0
NaNO$_3$	149.1	148.4	120.7
NH$_4$NO$_3$	102.9	101.6	98.7
LiNO$_3$	182.6	187.3	139.6
CsNO$_3$	96.6	95.2	...
RbNO$_3$	96.9	95.2	...
½ Ba(NO$_3$)$_2$	58.4	61.0	108.9
½ Sr(NO$_3$)$_2$	64.8	66.6	113.8
½ Ca(NO$_3$)$_2$	61.3	65.1	114.3

It is seen from column III. of this table that the solutions studied follow rather closely the rule, which has been previously stated,[1] that the osmose of the nitrates of the alkalies and alkaline earths varies inversely as the velocity of the cation divided by its valence. But the osmose does not seem to be proportional to the specific resistances of the solutions, as shown by comparing the values in column II. and those in column IV.

The rule which is tentatively advanced is that the amount of osmose of various salts with a common anion varies approximately inversely as the velocity of the cation divided by its valence.

There may be some connection between this phenomenon and the results obtained by Kohlrausch[2] and others in their work on the hydration of the ions.

Viewed in the light of this hypothesis of Kohlrausch the above experiments on the osmose of 0.001 normal nitric and acetic acids have additional interest. Here we have the fastest moving cation and two anions of very different velocities. As the flow of liquid is opposite to the direction of the current there can be no relation between the osmose and the

[1] This Journal, **36**, 28.
[2] P. Roy. Soc., **71**, 348.

resistances of the solutions. Besides, this negative flow is much greater in the case of acetic acid where the resistance is greater than with nitric acid.

IMPROVEMENTS IN MANOMETERS FOR THE MEASUREMENT OF OSMOTIC PRESSURE.[1]

By H. N. Morse and B. F. Lovelace.

We became convinced, in the course of our measurements during the past year, that the temperature coefficient of osmotic pressure could not be satisfactorily determined without a very considerable improvement in the method. The pressures which had been observed at 20° were so nearly equal to those found at 0° and 5°, and all of these differed so little from those we were finding at 10° and 15°, that the differences appeared to be covered by the possible errors of the work. The present year has therefore been largely spent in improving the method in every way which could contribute to the precision of the measurements.

The largest sources of error and uncertainty were connected with the construction of the cell and the manner of closing and opening it, and these were eliminated, first of all, by radical changes in the form of the cell and in its manometer attachments. The nature of the errors inherent in the old form of cell and the measures which were taken to correct them have been described in a former paper.[2]

Errors due to fluctuating temperature in the bath (*thermometer effects*) probably come next in the order of importance, and these were corrected by a system of automatic bath regulation which will be described in a later paper.

The present paper deals with improvements in the manometric portion of the work.

It is clear that, though a constant pressure which a solution is exerting may be, and often is, below the true maximum

pressure, or, under certain conditions, above it, the *correct determination* of that pressure depends principally on the reliability of the manometer, and that, on this account, it is impossible to give too much attention to the calibration, comparison, and testing of this instrument. Idiosyncrasies of the readers can be—and, in our practice, are—eliminated by the "check" system, according to which important readings at the telescope (and also at the polariscope) are made independently by two or more individuals.

The gas space in our manometers under atmospheric pressure is from 400 to 500 millimeters in length; hence, under the highest osmotic pressures (25–26 atmospheres) it may not have a length of more than 15 and a fraction millimeters, and the correction for meniscus alone may amount to more than 0.3 atmosphere. These facts will suffice to emphasize the care required in calibrating the tube, especially the upper end of it, and at the same time to explain the necessity of permanently filling with mercury all that portion of the top whose capacity has been affected by the operation of closing the manometer. Formerly, the introduction of this mercury was attended with considerable difficulties, which, however, have been overcome in the later method of filling the instruments. With equal care in calibration, a higher degree of accuracy could be secured by making the manometers longer, but it is not practicable to increase their length to any great extent, owing to the difficulty of obtaining long tubes which are sufficiently straight. Moreover, long tubes are much more likely to be broken by handling, and are less easily provided for in the bath.

The internal diameter of the manometer has remained from the first about 0.5 mm. Some advantage would be gained by using tubes of larger bore—especially in the greater distinctness of the meniscus—but whenever this has been tried, minute globules have become detached from the upper, stationary column of mercury, and it is often impossible to remove these from the glass and incorporate them with the mercury below. The same objection to large bore does not hold in the case of the *standard manometer* which is used only for

testing and verifying the others, and is not, therefore, subjected to so much rough usage as those which are put up with the cells. The standard manometer in use has an internal diameter of 2 mm.

Originally, the manometers were filled with dry air, but it was soon discovered that the volume of the enclosed gas gradually diminished, the decrease in some instances amounting to more than one per cent. It was assumed that the loss in volume must be due to impurities in the mercury which were attacked by the oxygen, though great pains had been taken in the purification of the mercury, and none of the appearances characteristic of the impure metal could be detected either on the mercury itself or on the glass tubes. The manometers were therefore filled with nitrogen instead of air. But it must not be overlooked that there is another possible explanation of the apparent diminution in gas volume, namely, a permanent stretching of the manometer under pressure, and any complete system of manometer control must include a provision for determining whether, and to what extent, a manometer is stretched—either temporarily or permanently—by the pressure to which it is subjected.

In determining capillary depression and the volume of the enclosed gas, and also in calibrating, the manometer must be joined to another glass tube, between which and the former there is free communication, and any lack of rigidity in the walls of the communicating channel gives rise to difficulties which are often very aggravating to the experimenter. But when manometers are to be compared with each other or with a standard, and when the question of stretching is to be investigated, absolute rigidity in this part of the apparatus is indispensable. The earlier forms of apparatus used by us were all imperfect in that they did not permit effective comparisons at pressures above 2 atmospheres. The apparatus which was devised during the past year, however, enables us to carry the investigation of the manometers up to pressures of 300 atmospheres. It is shown in section in Figure 1. It consists of a rectangular steel block which has been bored from end to end in the horizontal direction (*a*, Figure

1). Meeting the horizontal hole are two vertical holes, *b* and *c*. The latter serve as receptacles for two manometers which are to be compared or tested, one of which may be

FIG 1
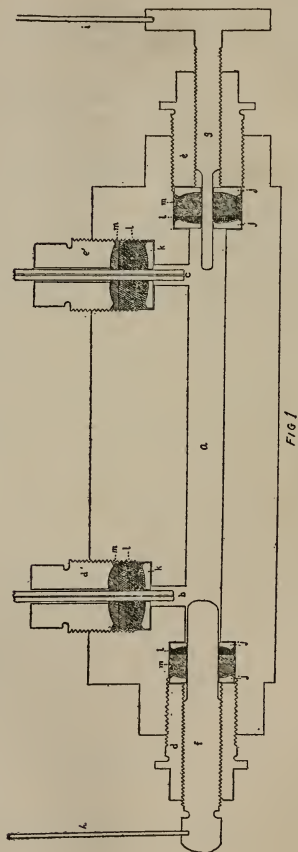
the standard manometer; or one may be occupied by a manometer and the other by a straight open tube, as in calibrating or in determining capillary depression, etc. At the ends of the block, the horizontal hole is bored out to a larger diameter and the wider parts are threaded to receive the steel plugs *d* and *e*, which hold the packing in place. The packing plugs are in turn bored and threaded to receive the plungers *f* and *g*, by means of which the pressure is regulated. The two plungers differ only in respect to size. One has nearly the diameter of the hole *a*, and serves for coarse adjustments; while the other is small, and is employed to effect slight changes in pressure. Both are operated by levers shown at *h* and *i*. The packing plugs in the vertical holes, *d'* and *e'*, are bored but not threaded, and their lower ends are concave in form.

The packing through which the plungers pass lies between two steel disks, *jj*, both of which are concave on the side facing the packing, except near the circumference, where they are cut back as shown in the figure. The purpose of the concave form of the disks is obviously to bring increased lateral pressure upon the plunger and thus prevent the leakage of mercury. A similar effect is produced in the opposite direction at the circumference by cutting back the edges of the disks. The arrangement in the vertical holes is similar. Here the packing also lies between two concave surfaces, one of which is furnished by the steel disk *k*, and the other by the plug *d'* or *e'*. It will be seen that any desired amount of pressure may be brought upon the packing by turning the plugs *d* and *e*.

The packing consists of rubber (*l, l, l,* and *l*) and leather (*m, m, m,* and *m*). The rubber is placed next the mercury in all packed regions in order to cleanse the advancing plungers or manometer tubes from any grease which may have been derived from the leather. If proper packing material is selected, and the packing plugs are screwed down tightly upon it, the pressure may be raised to 300 atmospheres without leakage of mercury or displacement of the glass tubes.

When a manometer tube is to be calibrated, it is drawn

out and bent over at the upper end, as shown in Figure 2. The lower part—including the two bulbs and the horizontal portion—is filled with mercury, and the instrument is then secured in its place in the steel block. In order to introduce the required calibrating thread, one of the plungers is turned until the tube, except a small space at the top, is filled with

FIG 2   FIG 3   FIG 5   FIG 6
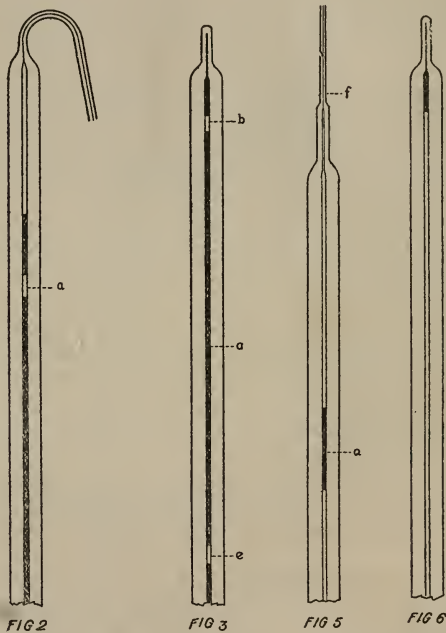
mercury. A small cup of mercury is then brought up to the open end, and the plunger is turned in the reverse direction until the required amount of metal has been introduced. This leaves the calibrating thread separated from the main column of mercury by an air space, as shown at *a* in Fig. 2. It is evident that both the air space and mercury thread can

easily be made of any desired length. The latter usually has a length of 12 to 15 millimeters.

By turning the plunger, the calibrating thread is brought down the manometer until its lower end reaches the line etched upon the glass which indicates the point at which the calibration is to begin, when the meniscus at both ends is developed by tapping the tube. The length of the space filled by the mercury thread is determined by means of the telescope and the standard meter. The thread is then raised until the bottom of the lower meniscus occupies quite exactly the former position of the top of the upper one, when the readings are repeated. Each movement of the mercury must, of course, be followed by a tapping of the tube until the form and the position of the meniscus become fixed; hence the exact setting of the thread requires some time, and always the coöperation of two persons, one of whom operates the plungers and taps the tube under the direction of the other, who is stationed at the telescope.

The calibrating thread is thus set end to end and its length determined, until the top of the tube is reached, when it is returned to the starting point and the operation is repeated. If the two records are found to be in accord at all points, the calibration is regarded as finished. If, on the other hand, discrepancies appear, the work is repeated until the different series of readings are harmonious throughout. It is then necessary only to reduce the readings and to plot a curve of corrections for the manometer.

The second step in the preparation of the manometer is to determine the correction for meniscus. This is done in the following manner: The calibrating thread is run out of the manometer and weighed and its volume is calculated. A long thread of mercury, which exactly fills the calibrated portion of the tube, is then introduced. This is also run out and weighed and its volume calculated. The difference between the volume of the long thread and that of the short one, multiplied by the number of settings, is clearly equal to all spaces which were not filled by the mercury when the calibrating thread was set end to end up the tube, and the

correction for a double meniscus will be found by dividing the total volume of this waste space by the number of settings less one.

The plan which is employed in investigating the stretching of manometers is most conveniently explained at this point, though the preparation of the tubes for that purpose cannot be understood until the method of filling the manometers has been described. Fig. 3 represents a calibrated tube which is to be tested. It will be noted that a long thread of mercury (*a*) is cut off from the mercury above and below by short spaces filled with air (*b* and *c*), or, better, with nitrogen. A tube, prepared as shown in the figure, is placed in the steel block, and the contents are subjected to any required pressure. It is obvious that, if stretching occurs, the imprisoned thread of mercury will shorten, and that the amount of the stretching can be determined, since all parts of the tube have been accurately calibrated. Moreover, it can be ascertained whether any observed stretching is temporary or permanent; for, if it is temporary, the thread will recover its original length when the pressure is removed. A permanent stretching of the manometer can also be detected, and the amount of it ascertained by redetermining, under a known pressure, the volume of the enclosed nitrogen.

The testing of a manometer by comparing it with the standard instrument is a simple operation which is employed to detect and correct errors of any kind, whether they are due to faulty calibration or a permanent stretching of the glass, or, possibly, to an incorrect previous determination of the volume of nitrogen. The standard manometer is made from heavier tubing, and has a larger bore than the instruments which are used with the cells, and every practicable measure is employed to insure its correctness. When a comparison is to be made, the standard is fixed in one of the receptacles of the steel block, and the manometer to be tested in the other. A series of equal pressures are brought upon the gas volumes of the two instruments, and the values of these, as determined by the standard, are compared with the pressures which are

calculated from the calibration data of the manometer under examination.

The comparison of any one manometer with another is precisely like its comparison with the standard. The occasion for such a comparison arises whenever the osmotic pressures which are found in the course of duplicate determinations appear to differ more widely than the other known sources of error in the method will justify.

The method of determining the capillary depression of a manometer presents no novel features. The open manometer is fixed in one of the receptacles of the steel block, and a tube with a broader upper part in the other, and the mercury is forced up until it enters the wider portion of the second tube. The difference in the level of the mercury in the two tubes is the capillary depression of the manometer. Since all of our manometers have about the same bore, *i. e.*, 0.5 mm., the correction for capillary depression is about constant, and varies but little from 0.02 atmosphere.

The nitrogen which is used to fill the manometers is obtained by passing air first through an alkaline solution of pyrogallol, and then, in the order named, over heated copper oxide, heated copper, heated copper oxide, calcium chloride, fused potassium hydroxide, and resublimed phosphorus pentoxide. The glass tubes containing the dry reagents are all connected with each other and with the receptacle for the nitrogen by fusing the ends together.

We have had occasion to answer many inquiries regarding our method of filling and closing manometers, which suggests that a somewhat detailed account of the procedure may be of use to others who are engaged in work with these instruments.

The arrangement of apparatus which is employed for the purpose is shown in Fig. 4. *A* is the reservoir for nitrogen; *B* is the calibrated manometer which is to be filled and closed; and *C* is an arrangement for filling and emptying the manometer. *B* is joined to *A*, at *d*, by fusing together the ends of the glass tubes and to *C*, at *e*, by means of rubber tubing. The mercury in *C* is separated from that in the manometer

by the air which nearly fills the wide tube below *e*. In this
way, the mercury in *C*, which may be impure from its contact

FIG 4
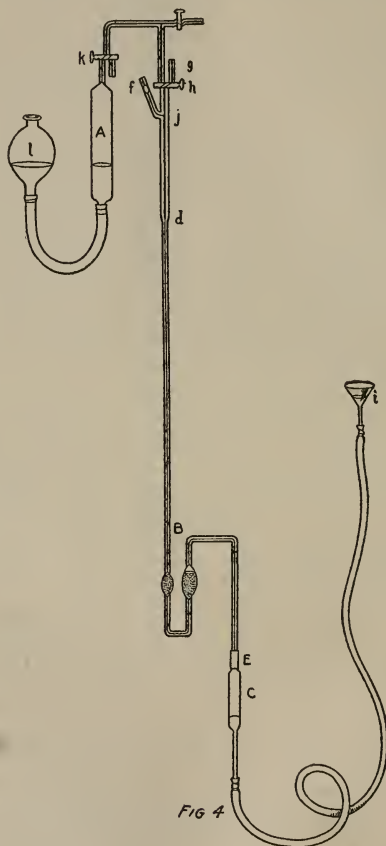
with rubber tubing, is prevented from ever entering the manom-
eter and contaminating the very pure mercury with which

that instrument is filled. This air also plays an important rôle when the manometer is closed.

Before joining the manometer B to A and C, its lower end is immersed in pure mercury and, with the instrument in an inclined position, gentle suction is applied at the other end until the two bulbs are filled with mercury. The introduction of the mercury in such a manner that the column between the two bulbs remains unbroken is an operation of some difficulty at first, but it is readily accomplished after a little practice. It is hardly necessary to state that the mercury which is used in manometers should never be allowed to come in contact with rubber.

The side tube f is closed with a short piece of rubber tubing and a screw pinchcock, and is connected with a drying apparatus. When the manometer is sealed to A at d, there is danger that some moisture from the flame will be deposited on the inside of the tube. To remove this, the tube is kept warm at d, while dried air is repeatedly introduced through f and expelled through g.

The next step is to fill the manometer with nitrogen from the reservoir A. The reservoir i is raised, and the air in the manometer is expelled through g, until the mercury column reaches the point j, when the stopcock h is closed and a small quantity of mercury is introduced into the side tube f. This is the mercury which is afterwards to occupy the upper end of the closed manometer. The rubber tube upon the end of f is now tightly closed, and the air remaining between j and the stopcock h is expelled through g, care being taken not to allow the mercury quite to reach the stopcock, lest it should be contaminated by some of the lubricating material on the latter. By turning the stopcocks h and k, and lowering i or raising l, the manometer is filled with nitrogen from A. This is wasted through g, and the manometer is again filled from A; and the operation of filling and emptying is repeated as often as may be thought necessary.

When the manometer has been filled for the last time, the reservoir i is adjusted to the right level and the gas is placed under very slightly increased pressure by raising the reser-

voir *l.* The stopcock *h* is opened to the air and instantly closed. This leaves the nitrogen in the manometer under a pressure equal to that of the atmosphere.

By gently pinching the rubber tube which closes *f*, a little mercury is forced out of the side tube into the vertical one between *j* and *d*; and by continuous tapping the small globules which separate at *j* from the thread in *f* are brought down the tube and made to collect above *d* in a continuous column. The mercury thus transferred from the side tube *f* to *d* does not enter the manometer, owing to the smallness of its bore.

The reservoir *i* is now lowered until all the mercury collected above *d* has been drawn into the manometer to a convenient distance below that point, when the glass at *d* is softened in the blowpipe flame, and the manometer is detached, but in such a manner as to leave both tubes sealed.

The glass at the closed end of the detached manometer is again softened in the flame, and the top of the tube is drawn out as shown in Fig. 5, that is, into a moderately wide capillary with thick walls below, and an *exceedingly* fine capillary above. After the tube has cooled down sufficiently, the column of mercury, *a*, Fig. 5, is forced upwards until it fills both capillaries, when the smaller one is fused off at *b* (under slightly diminished internal pressure), leaving the top of the manometer as shown in Fig. 6.

Great care is required in closing the manometer not to convert any considerable amount of the metal into vapor, and to heat the glass so uniformly that the vapor which is necessarily formed cannot recondense until the operation of closing is finished. Otherwise, the violent agitation of the mercury, due to rapid vaporization and condensation, is apt to shatter the tube.

Having filled and closed the calibrated manometer, the volume of the nitrogen, under standard conditions of temperature and pressure, must be ascertained. For this purpose, the instrument is placed in one of the receptacles of the steel block, and a long straight tube of equal bore in the other. The volume of the nitrogen is then found under several known

light pressures, and its volume under the standard pressure and at the standard temperature is calculated.

It remains only to compare the instrument with the standard manometer, but that operation has already been sufficiently described in connection with the uses of the steel block.

Johns Hopkins University,
June 1, 1908.

[Contributions from the Sheffield Laboratory of Yale University.]

CLIX.—RESEARCHES ON HALOGEN AMINO ACIDS: 3,5-DIBROMPHENYLALANINE.

[FOURTH PAPER.]

By Henry L. Wheeler and Samuel H. Clapp.

This paper may be considered as a preliminary contribution to the study of halogen substitution products of phenylalanine, or phenylaminopropionic acid. There appears to be no description of such substances in the literature of the acid. It is expected that a knowledge of the properties of these halogen derivatives, their stability toward reagents, etc., will prove of service in deciding the question of the position of halogens in protein substances.

The interesting and important work of Mörner[1] has shown that not only iodine[2] but also bromine and chlorine are widely met with in the skeletal tissue of the lower marine animals. Hundeshagen[3] previously found that all three halogens occur in organic combination in sponges, presumably, he states, in aliphatic amino acids or in tyrosine.

On account of Millon's test giving a negative result, Hofmeister[4] was the first to suggest that iodine enters the tyrosine molecule in iodalbumin. Blum and Vaubel[5] also expressed the view that iodine is combined in the tyrosine nucleus; that it does not replace the hydroxyl group but that, instead, it substitutes in the adjacent positions to this group. In the first

[1] Z. physiol. Chem., **51**, 33 (1907); **55**, 77 (1908).
[2] See also Harnach: *Ibid.*, **24**, 412 (1898); Mendel: Am. J. Physiol., **4**, 243 (1901); Cook: *Ibid.*, **12**, 95 (1905).
[3] Z. angew. Chem., **1895**, 475.
[4] Z. physiol. Chem., **24**, 159 (1898).
[5] J. prakt. Chem., **57**, 365 (1898).

paper of this series Wheeler and Jamieson[1] showed that Drechsel's iodgorgoic acid,[2] which is the only crystalline halogen amino acid that has yet been obtained from protein substances,[3] is in fact diiodtyrosine and not, as Drechsel supposed, iodaminobutyric acid.

Nürnberg[4] has recently published results, obtained by heating iodthyrin with water under pressure, which indicate that iodine substitutes in both the tyrosine and tryptophane molecules[5] in this substance.

On the other hand Oswald[6] has brought forward strong arguments to show that it is neither tyrosine nor tryptophane that exclusively contains the halogen. He suggested, however, that iodine enters exclusively or for the most part the aromatic groups and he concluded from his results and those of Pick,[7] in the case of the iodized proto- and heteroalbumoses, that phenylalanine is substituted by the halogen.

Several syntheses of phenylalanine have been devised, among which, perhaps, the two most practicable are the synthesis of Emil Fischer[8] and that of S. P. L. Sörensen.[9]

The first step in Fischer's synthesis is the preparation of benzylmalonic acid. It has been frequently observed when a benzyl halide containing negative groups is allowed to act on the monosodium salt of malonic ester that a dibenzyl- and not exclusively a monobenzylmalonic ester is formed. For example ortho- or paranitrobenzyl chloride reacts with the monosodium ethyl malonate to give, as chief product, a di(nitrobenzyl) malonic ester,[10] $(NO_2C_6H_4CH_2)_2C(CO_2C_2H_5)_2$.

In the present work we first observed that 3,5-dibrombenzyl bromide reacts in a similar manner and that di(3,5-dibrom-

[1] This Journal, **33**, 365; also Third Paper, *Ibid.*, **38** 356 (1907).

[2] Z. Biol., **33**, 90 (1896).

[3] See also Henze: Z. physiol. Chem., **38**, 360, and **51**, 64 (1907).

[4] Beitr. chem. Physiol. u. Path., **10**, 125 (1907).

[5] Compare Blum: Z. physiol. Chem., **24**, 159; Rhode: *Ibid.*, **44**, 161 (1905).

[6] Beitr. chem. Physiol. u. Path., **3**, 391, 413 (1903).

[7] Z. physiol. Chem., **24**, 246 (1898).

[8] Ber. d. chem. Ges., **37**, 3062.

[9] Compt. rend. Trav. Lab. Carlsberg, **6**, 6 (1902); Centrabl., **1903**, II., 33; Z. physiol. Chem., **44**, 448 (1905).

[10] Lellmann and Schleich: Ber. d. chem. Ges., **20**, 434 (1887).

benzyl)malonic ester, $(Br_2C_6H_3CH_2)_2C(CO_2C_2H_5)_2$, results as the chief product.[1]

It was then found that the elegant synthesis of Sörensen, which has been so successful in other cases, could also be used with the above benzyl bromide and that it gave an excellent yield of the desired dibromphenylalanine.

The new 3,5-dibrombenzyl bromide was prepared by adding bromine to 3,5-dibromtoluene at 170°–180°. The product thus obtained differed decidedly from the two possible isomeric tribromtoluenes;[2] the bromination had therefore taken place in the methyl group.

3,5-Dibrombenzyl bromide and the sodium salt of phthalimidomalonic ester reacted at 140°–150° as follows:

$$Br_2C_6H_3CH_2Br + NaC(CO_2C_2H_5)_2N(CO)_2C_6H_4 =$$
$$Br_2C_6H_3CH_2C(CO_2C_2H_5)_2N(CO)_2C_6H_4 + NaBr.$$

<div align="center">I.</div>
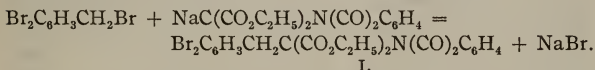
The 3,5-dibrombenzylphthalimidomalonic ester, I., when warmed with alkali and the solution acidified, gave the substituted malonic acid, II., which readily lost carbon dioxide, forming the phthalamic acid derivative, III. When this was heated with strong hydrochloric acid the phthalyl group was removed as phthalic acid and, on evaporating and treating the mixture with ammonia, 3,5-dibromphenylalanine, IV., was obtained. The yields, after the preparation of the benzyl bromide, were excellent.

<div align="center">

$Br_2C_6H_3CH_2C(COOH)_2NHCOC_6H_4COOH$

II.

$Br_2C_6H_3CH_2CH(COOH)NHCOC_6H_4COOH$

III.

$CH_2CH(NH_2)COOH$

</div>

<div align="center">IV.</div>
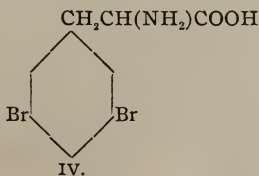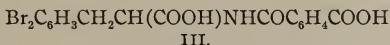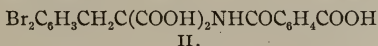
[1] The 3,5-dibrom compound is perhaps not the most probable naturally occurring bromine derivative of phenylalanine. We selected it as the first derivative for study, however, with the intention of eventually employing it in settling the structure of the halogen tyrosines.

[2] Nevile and Winther: Ber. d. chem. Ges., **13**, 974 (1880).

EXPERIMENTAL PART.

3,5-Dibrombenzyl Bromide,

$$
\begin{array}{c}
\mathrm{CH_2Br} \\
\end{array}
$$

(structure: benzene ring with CH_2Br at top, Br at lower left, Br at lower right) .—3,5-Dibromtoluidine
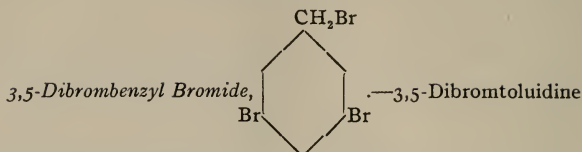
was prepared according to the directions of Klages and Liecke.[1] The amino group was then removed in the manner described by Jackson[2] and others in the case of tribromaniline.

Forty-two grams of dibromtoluene were heated in an oil bath at 170°–180° and to this one molecular proportion of bromine was added drop by drop. The contents of the flask were then cooled and the crystalline mass was extracted with hot 95 per cent alcohol. The substance remaining insoluble was nearly pure dibrombenzyl bromide since, after recrystallizing once from 95 per cent alcohol, it melted constantly at 95°–96°.

In another experiment 61 grams of 3,5-dibromtoluene at 175° and 42 grams of bromine, after extracting and crystallizing the product once from alcohol, gave a yield amounting to 45 per cent of the calculated.

3,5-Dibrombenzyl bromide crystallizes from 95 per cent alcohol in prisms, or long needles forming a feltlike mass. It is difficultly soluble in cold alcohol. It appears to be slightly volatile in the vapor of alcohol and it violently attacks the eyes. It was observed to boil unaltered at 173° at 19 mm. pressure and at 169° at 15 mm. pressure.

A determination of the replaceable bromine, of the side chain, was made by heating the substance in an alcoholic solution of sodium ethylate, evaporating to dryness, acidifying with nitric acid, and precipitating in the usual manner.

1.0257 gram of substance gave 0.5924 gram of AgBr.

0.3271 gram of substance gave 0.3104 gram of CO_2 and 0.0516 gram of H_2O.

[1] J. prakt. Chem. [2], **61**, 326 (1900).
[2] THIS JOURNAL, **12**, 167 (1890); **14**, 335 (1892).

	Calculated for $C_7H_5Br_3$.	Found.
Br	24.32	24.58
C	25.53	25.86
H	1.51	1.74

The mother liquors from the purification of the benzyl bromide gave a substance melting at 43°, probably 2,3,5-tribromtoluene.

Ethyl Phthalimidomalonate, $HC(CO_2C_2H_5)_2N(CO)_2C_6H_4$.—This was prepared according to Sörensen's[1] directions.

3,5-Dibrombenzylphthalimidomalonic Ethyl Ester, $Br_2C_6H_3CH_2C(CO_2C_2H_5)_2N(CO)_2C_6H_4$.—Twenty-seven grams of phthalimidomalonic ester were quickly added to a solution of the required amount of sodium ethylate in 300 cc. of dry alcohol, kept at about 40°. A clear, orange colored solution resulted, from which, on warming, the sodium salt separated as a yellow crystalline precipitate. The alcohol was then removed by distillation under reduced pressure, the last traces being removed finally by heating in an oil bath at 130° for three hours. Twenty-nine grams of dibrombenzyl bromide were then added (equal molecular proportions) and the mixture was heated at 140°–150° for 14 hours. At the end of the reaction the contents of the flask formed an oily mass, which, on cooling, hardened to a yellow crystalline cake.

The reaction product was then dissolved in boiling alcohol, and on cooling separated in stout prisms. The yield of pure substance was 39 grams, which is 80 per cent of the calculated.

As pointed out by Sörensen in other cases, the success of this synthesis depends largely on having the sodium salt of phthalimidomalonic ester free from water and alcohol. The ester should be very quickly mixed with the alcoholic sodium ethylate, as otherwise the salt frequently begins to separate before the addition of phthalimidomalonic ester is complete and the contents of the flask solidify to a gelatinous mass of the sodium salt, enclosing large quantities of unaltered ester. In one experiment in which the salt was heated with the benzyl bromide at 145° for only 3 hours, using 40.5 grams of

[1] *Loc. cit.*, or see Centrabl., **1903**, II., 33.

phthalimidomalonic ester, the yield of crude product was 64 per cent of the calculated.

3,5-Dibrombenzylphthalimidomalonic ethyl ester is insoluble in water, readily soluble in hot, and difficultly soluble in cold alcohol. It forms prisms and plates, often in aggregates. It melts at 144°–145° to a clear oil.

I. 0.2618 gram of substance gave 6.6 cc. moist N at 20° and 752 mm. pressure.

II. 0.0927 gram of substance required 1.8 cc. N/10 HCl.

III. 0.1574 gram of substance gave 0.1064 gram AgBr.

IV. 0.2249 gram of substance gave 0.1541 gram AgBr.

	Calculated for $C_{22}H_{19}O_6NBr_2$.	I.	II.	III.	IV.
				Found.	
N	2.53	2.85	2.72	....	....
Br	28.92	....	....	28.77	29.18

3,5-Dibrombenzylmalonicacidphthalamic Acid,

$Br_2C_6H_3CH_2C(COOH)_2NHCOC_6H_4COOH$.—For saponification, 30 grams of the above ester, finely pulverized, were suspended in 100 cc. of 5 N sodium hydroxide solution and warmed on the water bath for 6 hours. At the end of this time, the sodium salt had separated as a bulky mass difficultly soluble in the excess of alkali. Water was then added and, after filtering from a trace of unaltered ester, the free acid was precipitated by adding hydrochloric acid in slight excess to the cold solution.

The precipitate, which at first was oily, solidified on standing to a snow-white mass of prismatic crystals. A portion which remained floating on the supernatant liquid was removed and found to consist of well-developed prismatic forms, which began to lose carbon dioxide at about 110° with effervescence and in consequence possessed no sharp decomposition point. Nitrogen determinations agreed with the calculated values for a malonic acid derivative:

I. 0.4192 gram substance gave 10.2 cc. of moist N at 20° and 753.5 mm. pressure.

II. 0.2318 gram substance required 4.7 cc. N/10 HCl.

	Calculated for $C_{18}H_{13}O_7NBr_2$.	I.	II.
			Found.
N	2.71	2.76	2.84

Owing to the ease with which this substance loses carbon dioxide it could not be recrystallized. On boiling with water it readily loses carbon dioxide and is converted into:

3,5-Dibrombenzylaceticacidphthalamic Acid, $Br_2C_6H_3CH_2CH(COOH)NHCOC_6H_4COOH$.—This compound is the chief product obtained when the sodium salt above mentioned is acidified with hydrochloric acid without cooling. The yield is nearly quantitative. It was recrystallized by dissolving in warm alcohol, in which it is very soluble, and cautiously adding water to faint turbidity. It separated in dense clusters of minute prisms which melted to an oil, with considerable effervescence, at about 174°. It is almost insoluble in cold water.

I. 0.3530 gram substance gave 9.7 cc. moist N at 19° and 762 mm. pressure.

II. 0.1289 gram substance required 2.9 cc. N/10 HCl.

III. 0.1213 gram substance required 2.75 cc. N/10 HCl.

	Calculated for $C_{17}H_{13}O_5NBr_2$.	I.	Found. II.	III.
N	2.97	3.16	3.14	3.17

3,5-Dibromphenylalanine, $Br_2C_6H_3CH_2CH(NH_2)COOH$.—The foregoing derivative of phthalamic acid is readily saponified by boiling hydrochloric acid. Eighteen and one-half grams were finely pulverized and boiled with 20 per cent hydrochloric acid with a return condenser. Without apparently going into solution the powder was replaced by clusters of prismatic crystals and after continuing the boiling for 3 hours the saponification was complete. The solution was then concentrated to a volume of about 100 cc. and an equal volume of hydrochloric acid of specific gravity 1.19 was added. After standing some time the precipitate was filtered off and found to consist of a mixture of phthalic acid and the hydrochloride of 3,5-dibromphenylalanine.

In order to separate these acids the mass was dissolved in ammonia and the solution concentrated, whereupon the free dibromphenylalanine separated as a bulky mass, while the phthalic acid remained in solution. The yield corresponded

to 92 per cent of the calculated. The acid was recrystallized from water for analysis.

I. 0.2872 gram substance gave 0.3551 gram CO_2 and 0.0829 gram H_2O.

II. 0.1854 gram substance gave 7.2 cc. moist N at 770 mm. and 16.5°.

III. 0.2565 gram substance required 8.05 cc. N/10 HCl.

IV. 0.2043 gram substance required 6.6 cc. N/10 HCl.

V. 0.1748 gram substance gave 0.2023 gram AgBr.

	Calculated for $C_9H_9O_2NBr_2$.	I.	II.	Found. III.	IV.	V.
C	33.44	33.71	....	....	....	....
H	2.79	3.20	....	....	....	....
N	4.33	....	4.57	4.39	4.53	....
Br	49.53	....	....	....	....	49.25

3,5-Dibromphenylalanine is sparingly soluble in cold water but it dissolves in about 125 parts of water at 100°. It separates in long, hairy needles forming an extraordinary bulky mass, so that the beaker can be almost inverted. It is very sparingly soluble in boiling alcohol. Its aqueous solution tastes sweet and astringent. It melts with decomposition, to a red oil, at about 233°–234° when slowly heated. The point of decomposition depends considerably on the rate and manner of heating. It can be dried at 85°–90° but at 120° it gradually suffers decomposition.

Behavior of 3,5-Dibromphenylalanine toward Hydrochloric Acid and Barium Hydroxide.—3,5-Dibromphenylalanine can be heated for 6 hours in a sealed tube with hydrochloric acid (sp. gr. 1.19) at 130° apparently without suffering any significant decomposition.

Toward boiling concentrated solutions of barium hydroxide it is much less stable. When 0.3 gram of the acid was boiled with a barium hydroxide solution, saturated at 100°, for 8 hours, about eleven per cent of the bromine was found to have been removed, or in other words could be precipitated in nitric acid solution by adding silver nitrate.

The Dibromphenylalanine Hydrochloride,
$Br_2C_6H_3CH_2CH(NH_2HCl)COOH$.—3,5 - D i b r o m phenylalanine

dissolves slowly on boiling with 10 per cent hydrochloric acid, and on cooling separates in clusters of long prisms. On adding strong hydrochloric acid and continuing the boiling, the crystals, without apparently going into solution, are transformed into stout prisms which seem to have a different habit. When these were dried over sulphuric acid they had the composition of a 1:1 salt. They melted at about 254° with effervescence. Like the hydrochloride of diiodtyrosine the salt is dissociated by water.

0.2216 gram substance required 6.5 cc. N/10 HCl.

0.1553 gram substance gave 0.0618 gram AgCl.

	Calculated for $C_9H_9O_2NBr_2.HCl$.	Found.
N	3.89	4.11
Cl	9.87	9.84

Barium Salt, $[Br_2C_6H_3CH_2CH(NH_2)COO]_2Ba.3H_2O$.—This characteristic salt readily separates when barium chloride is added to a solution of the acid in ammonia. It is sparingly soluble in cold water but dissolves quite readily in water at 100° and separates slowly in clusters of thin, colorless plates or blades with curved outline.

The water determinations on the air dried substance agreed for a salt containing 3 molecules of water of crystallization.

0.1157 gram substance lost 0.0074 gram H_2O at 100°.

0.0567 gram substance lost 0.0035 gram H_2O at 100°.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Ba.3H_2O$	Found. I.	II.
H_2O	6.46	6.40	6.17

0.1081 gram substance dried at 100° gave 0.0320 gram $BaSO_4$.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Ba$.	Found.
Ba	17.58	17.42

Carbon dioxide produces no precipitate in an aqueous solution of this salt.

The *silver salt* was prepared by dissolving 3,5-dibromphenyl-alanine in the calculated quantity of one-tenth normal potassium hydroxide and then adding silver nitrate in excess. The silver salt separated in the form of microscopic crystals which remained perfectly white when dried at 80°. It was insoluble in boiling water. It dissolved in an excess of ammonia with ease and it was readily soluble in dilute nitric acid, especially on warming. It could be boiled for several minutes with nitric acid of sp. gr. 1.42 without separating silver bromide.

Copper Salt, $[Br_2C_6H_3CH_2CH(NH_2)COO]_2Cu.1^1/_2H_2O$. — This salt was prepared by adding copper sulphate to an aqueous solution of the acid. It formed light blue scales or irregular plates and it was almost insoluble in boiling water. Air dried, it contained one and one-half molecules of water of crystallization.

0.3056 gram substance lost 0.0113 gram H_2O at 90°.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Cu.1^1/_2H_2O$.	Found.
H_2O	3.67	3.70

0.0953 gram substance dried at 90° gave 0.0109 gram Cu_2S.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Cu$.	Found.
Cu	8.97	9.15

3,5-Dibromphenylalanine Ethyl Ester,
$Br_2C_6H_3CH_2CH(NH_2)COOC_2H_5$.—Five grams of finely pulverized dibromphenylalanine were suspended in absolute alcohol and dry hydrochloric acid gas passed through the solution to saturation without cooling. The substance rapidly went into solution. The solution was then evaporated to dryness under reduced pressure at a moderate temperature and the operation repeated. The alcohol was distilled off under reduced pressure, the crystalline residue taken up with cold water, and the free ester liberated with 33 per cent sodium hydroxide and shaken out with ether, while the solution was kept cold in a freezing mixture.

The ether extracts were shaken for 15 minutes with anhy-

drous potassium carbonate and then dried over sodium sulphate for 24 hours. The ether was distilled off and the ester distilled under diminished pressure. It boiled with very little decomposition and almost entirely between 234° and 237° at 24 mm. pressure. The weight of distilled ester collected was 4.2 grams, or 73 per cent of the calculated. This ester is a very thick oil with a faint, peculiar, aminelike odor. It is very difficultly soluble in water. For analysis is was converted into the picrate and the hydrochloride.

3,5-Dibromphenylalanine Ethyl Ester Picrate.—This substance separates when an aqueous solution of picric acid is added to an alcohol solution of the ester. It is very sparingly soluble in cold water but it dissolves in water at 100° and separates in large prisms which are irregular and very much etched. It melts at 181°–182° to a clear red oil, without significant effervescence.

I. 0.1163 gram substance required 8.1 cc. N/10 HCl.

II. 0.1388 gram substance required 9.6 cc. N/10 HCl.

	Calculated for $C_{11}H_{13}O_2NBr_2.C_6H_3O_7N_3$.	I. Found.	II.
N	9.66	9.75	9.68

3,5-Dibromphenylalanine Ethyl Ester Hydrochloride.—This was prepared by adding alcohol saturated with hydrogen chloride to the ester. It was very soluble in alcohol but it crystallized from a mixture of alcohol and ether in needlelike prisms. It melted to a clear oil at 186°–187°.

0.1320 gram substance gave 0.0492 gram AgCl.

0.1800 gram substance required 4.7 cc. N/10 HCl.

	Calculated for $C_{11}H_{13}O_2NBr_2.HCl$.	Found.
Cl	9.16	9.21
N	3.61	3.65

Di(3,5-dibrombenzyl)malonic Ethyl Ester,

$(Br_2C_6H_3CH_2)_2C(CO_2C_2H_5)_2$.—This compound is the chief product formed when 3,5-dibrombenzyl bromide and the sodium salt of ethyl malonate are allowed to act in molecular propor-

tions in alcoholic solution. After heating for one hour on the steam bath the solution no longer reacted alkaline to turmeric. The sodium bromide was then filtered off, the alcohol removed by distillation, and the residue was stirred with cold water. The yield of the undissolved substance was 60 per cent of the calculated. After one crystallization from alcohol it melted constantly at 99°. The ester is insoluble in water and dilute alkali and it crystallizes from alcohol in needlelike prisms.

I. 0.2639 gram substance gave 0.3077 gram AgBr.
II. 0.2323 gram substance gave 0.2679 gram AgBr.

	Calculated for $C_{21}H_{20}O_4Br_4$.	Found. I.	II.
Br	48.78	49.64	49.07

3,5-Dibrombenzylphthalimide, $Br_2C_6H_3CH_2N(CO)_2C_6H_4$.—This was obtained by heating equal molecular proportions of potassium phthalimide and 3,5-dibrombenzyl bromide for a short time at 140°. It crystallizes from alcohol in colorless prisms melting at 185°.

I. 0.0846 gram substance gave 0.0805 gram AgBr.
II. 0.2882 gram substance gave 0.2729 gram AgBr.
III. 0.2598 gram substance gave 8.5 cc. of moist nitrogen at 18°.5 and 762 mm. pressure.

	Calculated for $C_{15}H_9O_2NBr_2$.	I.	Found. II.	III.
N	3.54	3.77	....	....
Br	40.51	....	40.50	40.28

New Haven, Conn.,
    May, 1908.

CLX.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF 4-METHYLCYTOSINE.

[THIRTY-SEVENTH PAPER].

By Carl O. Johns.

There are two methyl derivatives of cytosine having the methyl group attached to carbon. Of these, 5-methylcytosine (Formula I.) has been described in the fifth paper of

this series,[1] while a description of the synthesis and properties of 4-methylcytosine (V.) will be given in the following pages.

Acetoacetic ester condenses readily in an aqueous solution of sodium hydroxide with pseudoethylthiourea hydrobromide to give an excellent yield of 2-ethylmercapto-4-methyl-6-oxy-pyrimidine (II.). This compound has been prepared by List[2] but his method requires several days, and, calculating from the weight of acetoacetic ester used, the yields are only about one-half as great as those obtained by the method here described.

When 2-ethylmercapto-4-methyl-6-oxypyrimidine is boiled with phosphorus oxychloride it yields 2-ethylmercapto-4-methyl-6-chlorpyrimidine (III.). When heated in a sealed tube at 140°–150° with alcoholic ammonia the chlorine in this compound is replaced by an amino group and 2-ethyl-mercapto-4-methyl-6-aminopyrimidine (IV.) is obtained. This is readily converted into 4-methylcytosine (V.) by digest-ing with concentrated hydrochloric acid and precipitating the base with a slight excess of ammonium hydroxide.

The chloride (III.) reacts more readily with alcoholic so-dium ethylate than it does with alcoholic ammonia. Action takes place at room temperature. Sodium chloride separates and 2-ethylmercapto-4-methyl-6-ethoxypyrimidine (VI.) is formed.

4-Methylcytosine can easily be distinguished from 5-methyl-cytosine. It does not melt at 310°, while 5-methylcytosine melts with effervescence at 270°. It is far less soluble in water than is 5-methylcytosine. Moreover, 4-methylcy-tosine crystallizes from water in long, anhydrous prisms, while 5-methylcytosine gives flat prisms containing one-half molecule of water.

4-Methylcytosine gives a very characteristic basic hydro-chloride containing 3 molecules of base to 1 molecule of hy-drogen chloride while 5-methylcytosine under similar con-ditions gives a hydrochloride containing 2 molecules of base to one of acid.

[1] Wheeler and Johnson: THIS JOURNAL, **31**, 591 (1904).
[2] Ann. Chem. (Liebig), **236**, 14 (1886).

When crystallized from concentrated solutions of the common acids, 4-methylcytosine gives a series of normal salts.

4-Methylcytosine has been used for the preparation of some purine derivatives to be described in another paper.

```
  N = CNH₂           HN — CO              N = CCl
  |      |           |     |              |     |
 OC    C.CH₃    C₂H₅SC   CH   →   C₂H₅SC   CH
  |      ||          ||    ||             ||    ||
 HN — CH            N — C.CH₃            N — C.CH₃
     I.                  II.                 III.

                                   ↙        ↓

  N = CNH₂           N = CNH₂            N = COC₂H₅
  |      |           |      |            |      |
 OC    CH   ←   C₂H₅SC   CH        C₂H₅SC   CH
  |      ||          ||     ||           ||     ||
 HN — C.CH₃         N — C.CH₃           N — C.CH₃
     V.                 IV.                 VI.
```

EXPERIMENTAL PART.

2-Ethylmercapto-4-methyl-6-oxypyrimidine,
```
       HN — CO
       |     |
 C₂H₅SC   CH  .
       ||    ||
       N — C.CH₃
```
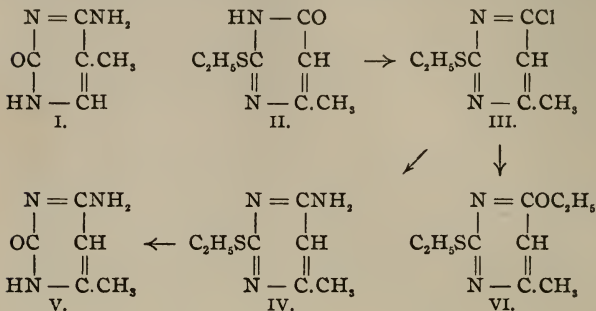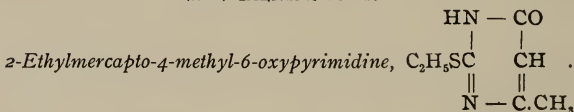
—List[1] prepared this compound by heating 2-thio-4-methyl-6-oxypyrimidine with ethyl iodide in the presence of sodium ethylate. It can be obtained more easily and in better yields by condensing pseudoethylthiourea hydrobromide with acetoacetic ester in an aqueous solution of sodium hydroxide. This condensation is very smooth and the yields range from 80 to 90 per cent of the theoretical quantity.

Ninety-three grams of pseudoethylthiourea hydrobromide are dissolved in 100 cc. of water and this solution is mixed with 65 grams of acetoacetic ester. To this mixture is slowly added a solution of 40 grams of sodium hydroxide in 80 cc. of water. Condensation takes place at once, but to insure complete reaction the mixture is allowed to stand at room temperature overnight. When the resulting clear solution

[1] Ann. Chem. (Liebig), **236**, 14 (1886).

is acidified with acetic acid about 75 grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine are obtained. When crystallized from dilute alcohol it melts at 144°–145° and possesses all the properties of List's compound.

Analyses (Kjeldahl):

	Calculated for $C_7H_{10}ON_2S$.	I.	II.
N	16.47	16.49	16.52

2-Ethylmercapto-4-methyl-6-chlorpyrimidine,

$$C_2H_5SC \begin{array}{c} N = CCl \\ | \quad\quad | \\ CH \\ || \quad\quad || \\ N - CCH_3 \end{array}.$$
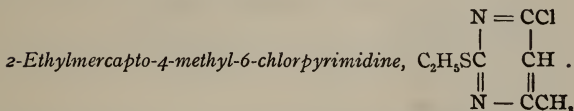
—Twenty grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine were heated with 60 cc. of phosphorus oxychloride in an oil bath kept at 130°–135° until hydrogen chloride was no longer evolved. The excess of phosphorus oxychloride was removed under diminished pressure and the resulting thick oil was poured on cracked ice. The chloride was extracted with ether and dried over calcium chloride. When the ether was evaporated a clear, red oil remained. This boiled at 142° at 15 mm. pressure. The yield of pure chloride was about 75 per cent of the calculated quantity. This chloride is very stable towards water and alcohol.

Analyses (Kjeldahl):

	Calculated for $C_7H_9N_2SCl$.	I.	II.
N	14.85	14.71	15.09

2-Ethylmercapto-4-methyl-6-ethoxypyrimidine,

$$C_2H_5SC \begin{array}{c} N = COC_2H_5 \\ | \quad\quad | \\ CH \\ || \quad\quad || \\ N - CCH_3 \end{array}.$$
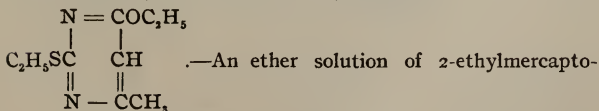
—An ether solution of 2-ethylmercapto-4-methyl-6-chlorpyrimidine was added to alcohol containing an excess of sodium, calculating from the chloride. An immediate reaction took place with the liberation of heat.

The excess of alcohol was evaporated, and, after adding
water, the oil was shaken out with ether and dried over cal-
cium chloride. When the ether was evaporated an oil re-
mained. This boiled at 154° at 20 mm. pressure.

Analyses (Kjeldahl):

	Calculated for $C_9H_{14}ON_2S$.	Found.	
		I.	II.
N	14.14	14.08	14.43

2-Ethylmercapto-4-methyl-6-aminopyrimidine,

$$\begin{array}{c} N = CNH_2 \\ | \quad\quad | \\ C_2H_5SC \quad CH \\ || \quad\quad || \\ N - CCH_3 \end{array}$$
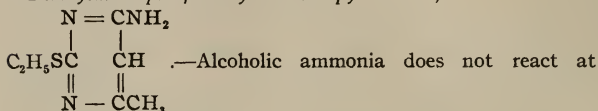
.—Alcoholic ammonia does not react at
room temperature with 2-ethylmercapto-4-methyl-6-chlorpyr-
imidine. Sixteen grams of the chloride were heated in a sealed
tube for 4 hours at 140°–150° with about 75 cc. of alcoholic
ammonia saturated at 0°. The tube, wheen cooled, was
lined with ammonium chloride and crystals of the new amino
compound. The reaction was very smooth and the alcohol
remained colorless. After evaporating to dryness, the resi-
due was washed with cold water and recrystallized from di-
lute alcohol. The crystals melted at 115°–116° to a clear
oil. They have a tetrahedral outline and show a great ten-
dency to twin. They are easily soluble in cold alcohol and
acetic acid, moderately soluble in cold benzene, and diffi-
cultly soluble in boiling water.

Analyses (Kjeldahl):

	Calculated for $C_7H_{11}N_3S$.	Found.	
		I.	II.
N	24.85	24.83	25.07

4-Methylcytosine,

$$\begin{array}{c} N = CNH_2 \\ | \quad\quad | \\ OC \quad CH \\ | \quad\quad || \\ HN - CCH_3 \end{array}$$
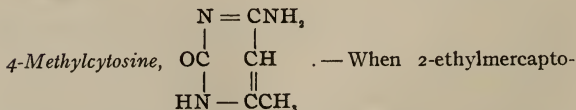
.— When 2-ethylmercapto-
4-methyl-6-aminopyrimidine is evaporated with concentrated
hydrochloric acid ethyl mercaptan is evolved and an almost

theoretical yield of 4-methylcytosine monohydrochloride is obtained. The base is obtained from this salt by adding an excess of ammonium hydroxide. 4-Methylcytosine crystallizes from water in anhydrous, slender, brittle prisms. These crystals do not melt at 310°, but decompose slowly without effervescence at higher temperatures. 4-Methylcytosine is moderately soluble in boiling water. At 24°, 0.36 gram is dissolved by 100 cc. of water. It is soluble in cold aqueous ammonia and in cold acetic acid.

Analyses (Kjeldahl):

	Calculated for $C_5H_7ON_3$.	I.	II.
N	33.60	33.52	33.39

4-Methylcytosine Monohydrochloride, $C_5H_7ON_3.HCl$.—This salt is obtained when 2-ethylmercapto-4-methyl-6-amino-pyrimidine is digested with concentrated hydrochloric acid. It is also formed by crystallizing 4-methylcytosine from 20 per cent hydrochloric acid. It is moderately soluble in hot hydrochloric acid and separates on cooling in blunt, flat prisms with a hexagonal appearance. When dried over potassium hydroxide it does not lose water at 110°. In a capillary tube it begins to shrivel at about 280° and decomposes slowly above 300°.

Analyses:

	Calculated for $C_5H_7ON_3.HCl$.	I.	II.
N	26.00	26.10	26.09
Cl	21.98	21.81	....

The anhydrous monohydrochloride of 4-methylcytosine is also obtained unaltered when its aqueous solution is saturated with hydrogen chloride and evaporated in a desiccator. The crystals thus obtained did not lose weight at 125°.

Analysis:

	Calculated for $C_5H_7ON_3.HCl$.	Found.
Cl	21.98	21.95

4-Methylcytosine Basic Hydrochloride, $(C_5H_7ON_3)_3.HCl$.— Such a salt was formed when a hot aqueous solution of 0.25

gram of the base was mixed with an aqueous solution of 0.32 gram of the monohydrochloride. The basic salt separated in scales with a pearly lustre. These began to shrivel at about 270° and turned brown above 280° but did not melt at 310°. These crystals lost weight when dried at 130°–140°, but attempts to determine water of crystallization gave results that differed widely, but indicated that one molecule of water was probably present. The dried salt contained 3 molecules of the base and 1 molecule of hydrogen chloride. This same salt was obtained when equal weights of the base and monohydrochloride were recrystallized from water.

Analyses of the dried salt:

	Calculated for $(C_5H_7ON_3)_3$.HCl.	I.	Found. II.	III.
N	30.61	....	30.26	....
Cl	8.62	8.51	.....	8.49

4-Methylcytosine Nitrate, $C_5H_7ON_3$.HNO_3.—One-half gram of 4-methylcytosine was crystallized from 10 cc. of 25 per cent nitric acid. The salt separated in round clusters of blunt prisms. It did not contain water of crystallization.

0.0983 gram of substance gave 25.2 cc. of moist nitrogen at 18° and 770 mm. pressure.

	Calculated for $C_5H_7ON_3$.HNO_3.	Found.
N	29.79	29.94

4-Methylcytosine Sulphate, $(C_5H_7ON_3)_2$.H_2SO_4.H_2O.—When 4-methylcytosine was crystallized from 25 per cent sulphuric acid, two molecules of the base united with one molecule of sulphuric acid to form a normal sulphate containing one molecule of water of crystallization. The crystals were large, flat prisms that did not lose water at 110°, but lost one molecule of water slowly at 160°–170°.

Analyses:

	Calculated for $(C_5H_7ON_3)_2$.H_2SO_4.H_2O.	I.	Found. II.	III.
H_2O	4.91	....	4.83	....
N	22.95	22.79	....	22.82
S	8.74	....	8.88	....

4-Methylcytosine Picrate, $C_5H_7ON_3.C_6H_2(NO_2)_3OH$.—When an aqueous solution of picric acid is added to a solution of 4-methylcytosine, an immediate precipitate is obtained. This picrate is difficultly soluble in hot water and crystallizes in beautiful, yellow needles that turn brown at about 265° and decompose slowly above that temperature.

0.0858 gram of substance gave 17.3 cc. of moist nitrogen at 18° and 772 mm. pressure.

	Calculated for $C_5H_7ON_3.C_6H_2(NO_2)_3OH$.	Found.
N	23.73	23.65

New Haven, Conn.,
May, 1908.

THE CONDUCTIVITY AND IONIZATION OF ELECTROLYTES IN AQUEOUS SOLUTIONS AS CONDITIONED BY TEMPERATURE, DILUTION, AND HYDROLYSIS.

By Harry C. Jones and C. A. Jacobson.

Introduction.

It is now generally recognized that chemical activity is conditioned primarily by the number of reacting parts or ions. Therefore, any method by which the number of ions can be determined or, in other words, any method that gives the percentage dissociation of a compound, is of fundamental importance. Of the three or four methods now in use for determining ionization, the electrical conductivity method is doubtless the most general, and possibly the most reliable.

That the conductivity of electrolytes is influenced by temperature has been known for about fifty years.

Beetz,[1] in 1862, was the first to arrive at any definite relation between temperature and conductivity, although Hankel,[2] Marie-Davy,[3] Becquerel,[4] and a few others had previously made some observations which led them to conclude that the conductivity of electrolytes increases with rise in tempera-

[1] Pogg. Ann., **117**, 1 (1862).
[2] *Ibid.*, **69**, 255 (1846).
[3] Compt. rend., **54**, 465.
[4] Pogg. Ann., **70**, 254 (1847).

ture. Beetz worked with zinc sulphate from 1° to 24°, at various concentrations, and arrived at the formula

$$Z = 32.09 + 4.0346p - 0.04073p^2$$

as expressing the relation between temperature and conductivity. (p is the percentage concentration of anhydrous zinc sulphate.) He thus concluded that the conductivity increases proportionally with rise in temperature, except at high dilutions. Beetz also observed a maximum in the conductivity curve, with changing concentration, and noticed that this maximum varied with change in temperature. In 1879 Freund[1] repeated the experiments of Beetz and found the same relations to hold, but his results were about 5 per cent higher. Other investigators in this field are: Berggren,[2] Lentz,[3] and Sack.[4] The last-named found a sharp maximum conductivity in three different concentrations of copper sulphate.

Grotrian,[5] in 1874, investigated the effect of temperature on the conductivity of sulphuric and hydrochloric acids, from 8° to 70°, at different dilutions, and concluded that conductivity is a linear function of the temperature. The following year Kohlrausch and Grotrian[6] made a comprehensive study of this field, using numerous salts and acids at temperatures ranging between 0° and 40°, and deduced the following formula as expressing the relation between temperature and conductivity:

$$K_t = K_0(1 + \alpha t + \beta t^2),$$

in which K represents the conductivity, t the temperature, and α and β constants of different orders of magnitude, as found by experiment. They calculated the temperature coefficients at 18° by the equation

$$\left(\frac{1}{K}\frac{dK}{dt}\right)_{18} = \frac{\alpha + 2\beta.18}{1 + \alpha.18 + \beta.18^2},$$

[1] Wied. Ann., **7**, 49 (1879).
[2] *Ibid.*, **1**, 499 (1877).
[3] Bull. Acad. Imp. Sci., St. Petersb., **10**, 299.
[4] Wied. Ann., **43**, 212 (1891).
[5] Pogg. Ann., **151**, 378 (1874).
[6] *Ibid.*, **154**, 215 (1875).

in which the symbols have the same meaning as above. From this work they concluded that the conductivity of dilute solutions is not a linear function of the temperature, as was originally thought, but a *parabolic one.* They also observed a maximum conductivity for hydrochloric acid when the concentration was about 30 per cent. In 1885 Kohlrausch[1] represented conductivity graphically as the cube root of the concentration. In other words, he made μ_v the ordinate and $\sqrt[3]{\mathrm{1/v}}$ the abscissa.

Up to this time no exception had been found to the general principle that the conductivity of electrolytes in aqueous solution increases with rise in temperature, and also with increase in dilution where the concentration is less than 0.1 normal. Arrhenius,[2] in 1889, was the first to notice an exception. He found that the conductivity of phosphoric and hypophosphorous acids decreases with rise in temperature, between 25° and 95°. Sack[3] and others have since observed negative temperature coefficients, but more especially with organic solvents. The explanation hitherto offered for the rapid increase in conductivity with rise in temperature is that dissociation increases as the temperature increases. In other words, the higher the temperature the larger the number of ions present for a given concentration and, consequently, a resulting increase in conductivity. The fact that Arrhenius found a diminishing dissociation with rise in temperature led others to work along this line.

In 1890 Krannhals[4] took up the problem and measured the conductivity of a number of acids and salts at the following temperatures: 18°, 50°.3, 82°, and 99°.4. He found that the conductivity increases as a linear function of the dilution, and a parabolic function of the temperature, except for magnesium sulphate and potassium ferrocyanide, where the increase is abnormally great. The reason for this increase in conductivity with rise in temperature he ascribed to diminishing viscosity of the solvent. In some cases he

[1] Wied. Ann., **26**, 197 (1885).
[2] Z. physik. Chem., **4**, 96 (1889).
[3] *Loc. cit.*
[4] Z. physik. Chem., **5**, 250 (1890).

observed a decrease in dissociation with rise in temperature, but concluded that this must be due to experimental error.

The same year J. Trötsch[1] undertook an investigation to ascertain the influence of water of crystallization on the conductivity of electrolytes, and arrived at the conclusion that the conductivity of those substances which do not crystallize with water increases regularly or remains constant with rise in temperature, while in the case of those substances that crystallize with water, the rate of increase of conductivity grows less as the temperature rises, as well as with increase in dilution. He also noticed that the temperature coefficients of cupric chloride, at all concentrations, increase from 0° to 40°, and then decrease. He noticed a sudden change in color from green to blue in an 18.2 per cent solution of cupric chloride, and from red to blue at different concentrations of cobalt chloride above 100°. He explained these phenomena as being due to a loss of the water of hydration. He also concluded, as many before him had done, that increase in temperature increases the dissociation.

In 1891 Douglas[2] worked with several acids, bases, and salts at temperatures ranging from 0° to 35°. From his work he drew the conclusion that dissociation is independent of temperature. The same conclusion was reached by Wood[3] and Jahn,[4] although the results of the former indicate just the opposite. Jahn, however, admitted that his results, in the case of valeric acid, showed a diminishing dissociation with rise in temperature, but thought that this was probably due to experimental error.

In 1900 Whetham[5] determined the ionization of a few strongly dissociated acids and salts at 0° by the freezing point method. After comparing his results with those of Kohlrausch, he concluded that the dissociation is greater at 0° than at 18°.

[1] Wied. Ann., **41**, 259 (1890).
[2] This Journal, **26**, 428 (1891).
[3] Phil. Mag., **41**, 117 (1896).
[4] Z. physik. Chem., **16**, 72 (1895).
[5] *Ibid.*, **33**, 344 (1900).

The more recent investigations of Euler,[1] Schaller,[2] Noyes,[3] and West,[4] however, all point to the conclusion that dissociation diminishes with rise in temperature. Euler worked with a number of organic acids at eight temperatures ranging between 0° and 50°. Schaller studied organic acids and salts at temperatures ranging between 25° and 99°. In addition to observing that dissociation decreases with rise in temperature, he noticed that when the electrolytes are completely dissociated, the increase in conductivity is very nearly a linear function of the temperature. This was contrary to the observation of Kohlrausch and Grotrian referred to above.

An enormous amount of conductivity work has been done besides that already mentioned, but no reference will be made to work carried out at only one temperature, or where solvents other than water have been used, since that would not properly come within the scope of this paper.

We may summarize the results hitherto obtained as follows:

(1) The conductivity increases with rise in temperature.

(2) Conductivity increases with increase in dilution.

(3) Dissociation increases with increase in dilution.

Considering the number of conflicting results on the following points, we are inclined to believe that further confirmatory evidence is necessary before some of them are fully established:

(1) Dissociation decreases with rise in temperature.

(2) Conductivity is a linear function of the temperature.

(3) Conductivity is a cube root function of the concentration.

Some time after the publication of West's work, Jones[5] pointed out certain relations existing between the temperature coefficients of electrolytes and their hydrating power. Using West's results he showed that those electrolytes with no hydrating power have smaller temperature coefficients than those with large hydrating power, and that the order

[1] Z. physik. Chem., **21,** 257 (1896).

[2] *Ibid.,* **25,** 497 (1898).

[3] J. Am. Chem. Soc., **26,** 134 (1904).

[4] This Journal, **34,** 357 (1905).

[5] *Ibid.,* **35,** 445 (1905).

of the temperature coefficients will, in a measure, determine the hydrating power of the electrolyte. The close relation existing between the water of hydration and water of crystallization of a compound is seen from the work of Jones and his students.[1]

Purpose of this Investigation.

From the brief historical sketch here given, it is seen that the conclusions drawn regarding the influence of temperature upon dissociation are very conflicting, and that they need further experimental verification before they can be considered as fully established. The present work was undertaken to supply some such evidence; and, further, to extend the investigation to a larger number of inorganic compounds than was done by West, as well as to include some typical organic acids, to test the relations pointed out by Jones[2] between the temperature coefficients of conductivity of electrolytes and their hydrating power.

Method Employed.

The present work is, broadly speaking, a continuation of that by Jones and West,[3] and the method is essentially the same as the one that they employed.

Apparatus.—Eight conductivity cells of the form used in this laboratory were employed. The conductivities were read at eight concentrations, ranging from N/2 to N/2048, according to the Ostwald scheme of dilution. One cell was employed for each dilution.

The well-known Kohlrausch method, consisting of a Wheatstone bridge, resistance box, telephone, and an induction coil supplying the alternating current, was employed for reading the conductivities. The calibration of the bridge wire, resistance box, and thermometers was done in essentially the same way as that described by Jones and West. Moreover, it was considered advisable to keep the same range of temperature as they did, namely 0°, 10°, 25°, and 35°.

[1] Carnegie Monograph No. 60 (Hydrates in Solution), 1906.
[2] This Journal, **35**, 445 (1905).
[3] *Ibid.*, **34**, 357 (1905).

In order to bring the cells containing the solutions to these temperatures, constant-temperature water baths were employed. We found that the zero bath described by West

Fig. 1.
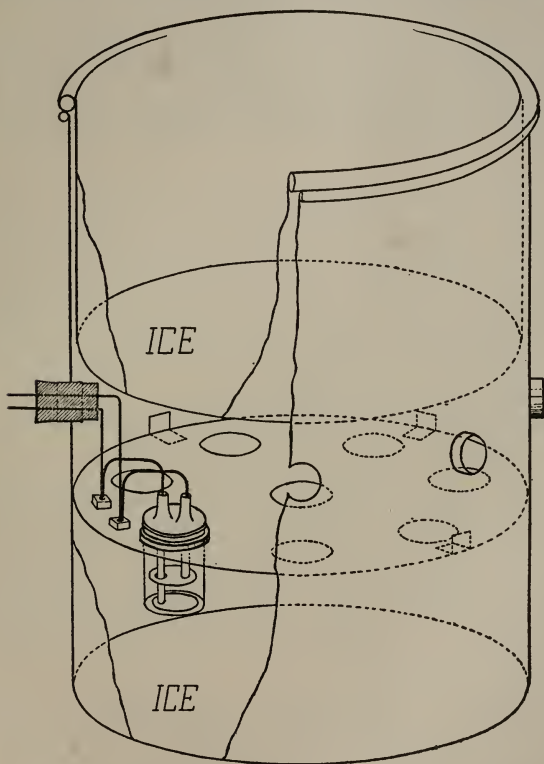
gave conductivities that were invariably too high by about 0.5 per cent, and the difficulty was thought to lie in the fact that the upper portion of the cell was exposed to a much

higher temperature, and, consequently, heat would be conducted into the solution, especially by the mercury of the electrodes. To overcome this difficulty, we constructed another form of ice bath, shown in the accompanying cut, Fig. I. By this means the air above and in immediate contact with the cells could also be brought to zero temperature. The whole apparatus was surrounded by hair packing, and well protected against conduction of heat from surrounding objects. This form of ice bath gave entirely satisfactory results.

The temperature of the 10° bath was regulated by a small gas burner and running hydrant water, stirred by a hot-air engine. We found that the temperature of the hydrant water did not remain constant long enough to answer our purpose without this regulation. Instead of using the Ostwald thermoregulator for the 25° and 35° baths, as was done by West, we obtained better results by simply regulating the flame of a small gas burner by hand. The water in these two baths was also stirred as above indicated.

The burettes and measuring flasks were calibrated for 20° by weighings reduced to the vacuum standard.

Water.—The conductivity water employed in this laboratory[1] was used in preparing the solutions. In order to obtain the true value for the conductivity of the electrolyte, a correction term must, of course, be applied for the conductivity of the solvent. Where the dilution is high this correction has a considerable value. The temperature coefficients of conductivity of water are also large, and this fact must be taken into account wherever conductivities are read at more than one temperature.

Although the marked influence of temperature on the conductivity of water had been pointed out by Pfeiffer[2], Kohlrausch,[3] and Schaller,[4] yet very few of the experimenters working in this field state that this fact was taken into account.

[1] This Journal, **19**, 91 (1897).
[2] Wied. Ann., **31**, 831.
[3] Z. physik. Chem., **14**, 324 (1894).
[4] *Ibid.*, **25**, 497 (1898).

Euler[1] gives his reason for not applying the correction for water. Kohlrausch and Heydweiller found that the increase in the conductivity of water with rise in temperature was more rapid at higher than at lower temperatures. Schaller's results indicate a linear relation between conductivity and temperature from 25° to 99°. The latter relation has been found to hold in our work with numerous samples of water. A few of the results obtained with water investigated during the progress of this work are plotted in the accompanying diagram, where temperatures are the abscissae, and conductivities $\times 10^{-6}$ the ordinates.
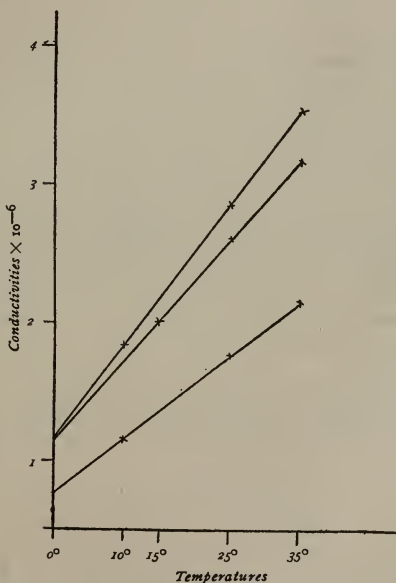
Fig. II.

Solutions.—The purest obtainable materials were used in the preparation of the solutions. However, before the

[1] *Loc. cit.*

salts were used they were carefully tested for impurities, and in most cases recrystallized one or more times. Except in a few cases, where the compounds are stable in the air, the solutions were all standardized by analysis. The organic acids, the purity of which had first been tested by determining their melting points, were standardized volumetrically with an aqueous solution of potassium hydroxide, which had been especially prepared and purified. The solutions were then made up by diluting the more concentrated with water, and bringing them to the calibration temperature.

Cell Constants.—For determining the cell constants, we took ($129.7 + \mu$ for water) as the conductivity of a N/50 solution of potassium chloride at $25°$ as the basis of our calculations. The purest obtainable potassium chloride was tested and further purified by fractional crystallization before it was used in the preparation of the above-mentioned standard solution. With this solution the cell constants of the first four cells were determined. Then a N/500 solution was prepared from the N/50 and its conductivity found by using the four cells whose constants had been determined. The value thus obtained for μ of the more dilute solution was used in determining the cell constants of the remaining four cells. The cell constants were redetermined every three or four weeks throughout the year. Ordinarily, no change in the cell constants amounting to more than 0.2 to 0.3 per cent was found.

For the purpose of checking the cell constants at $0°$, we determined the following values of μ for potassium chloride: N/500 at $25° = 137.7$, N/50 at $0° = 71.45$, N/500 at $0° = 75.63$. These are the averages of a large number of determinations, none of which varied more than 0.5 per cent from the others. To obtain the true values for any one of these solutions, the proper value for μ of water must be added.

Units.—To be consistent with the work previously done in this laboratory the results are expressed in Siemens units, and all conductivities here referred to are molecular conductivities—gram-molecular weights having been used in making up the solutions.

Results.—The results are expressed in the following tables. The molecular conductivities (μ_v) at the four temperatures indicated were calculated from the equation

$$\mu_v = K \frac{Va}{Rb}$$

where K is the cell constant, V the volume concentration, R the resistance, a and b the two arms of the bridge. The percentage dissociation (α) was calculated from the equation

$$\alpha = \frac{100 \cdot \mu_v}{\mu_\infty},$$

where μ_∞ is the conductivity at complete dissociation, or the highest value for μ_v obtained for the strongly dissociated electrolytes in which no hydrolysis is known to have taken place. When hydrolysis did take place, as, for example, with ferric chloride, as well as in the case of the weakly dissociated organic acids, α was calculated from Kohlrausch's law, $\mu_\infty = c + a$, where c and a represent the velocities of the cation and anion, respectively. The temperature coefficients, expressed in conductivity units between the temperatures indicated, were calculated from the formula

$$\frac{(\mu_v)_{t_1} - (\mu_v)_t}{t_1 - t},$$

in which $(\mu_v)_{t_1}$ represents μ_v at the higher temperature (t_1) and $(\mu_v)_t$ at the lower temperature (t), while the same coefficients expressed in percentages were calculated from the formula

$$\frac{(\mu_v)_{t_1} - (\mu_v)_t}{t_1 - t} \times \frac{100}{(\mu_v)_t}.$$

For each conductivity measurement given in the tables, three readings were taken, changing the resistance in the resistance box so as to bring the node on the bridge as near to the 40, 50, and 60 cm. marks as practicable. The mean of these was taken as the final reading. Whenever any ir-

regularities appeared, either in the conductivities or in the temperature coefficients, the same readings were repeated one or more times on following days.

Sources of Error.

It may be well to call attention to some of the more important sources of error that must be taken into account in all conductivity work. In the first place, a sharp minimum in the telephone is not secured unless the electrodes are clean and well covered by a layer of platinum black or "platinum white." A small amount of an oily constituent is present in ordinary distilled water, and where the electrodes are left overnight in such water a small residue will be left on them, as is often seen deposited on the inside walls of washbottles, etc. It may take weeks before this becomes perceptible, but it should be taken into account.

At temperatures above 25° air bubbles are often found to gather on the electrodes, as has been pointed out by Jones and West. These not only interfere with the minimum in the telephone but may also affect the conductivity. After trying various methods for obviating this difficulty we found that the most satisfactory one was to heat the bath a few degrees above the temperature at which the conductivities are to be read, and after the bubbles have collected for a time, to raise the electrodes out of the solution, then returning them at once and cooling down the bath to the required temperature. When this is done the cells may be kept for any desired length of time at the temperature in question without any sign of a bubble appearing.

Another source of error often arises in assuming that the cells have attained the temperature of the bath before they have actually done so.

When small resistances are to be measured it is of the utmost importance to have the plugs in the resistance box absolutely clean, since a very small quantity of foreign matter on a plug will accumulate on the small resistance read, and will often amount to several per cent.

When working at temperatures above that of the room, a source of error that must not be overlooked is the condensation of the solvent on the glass stopper of the cell, thus concentrating the solution.

A formidable source of error is found in hydrolysis taking place to a greater or less extent in dilute solutions. This, of course, increases the conductivity to an enormous extent, as is seen especially in the case of iron salts. For this reason it becomes impossible to find μ_∞ for such compounds by the conductivity method directly, and the true value of μ_∞ for other electrolytes is called into question, since we are unable to tell to what extent hydrolysis has taken place.

Lithium Chloride.

Table I.—Molecular Conductivity and Dissociation.

	0°.		11°.2.		25°.		35°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	41.33	72.1	55.26	70.3	75.79	68.7	91.71	68.5
8	47.27	82.4	64.18	81.6	88.41	80.1	105.9	79.1
16	49.20	85.8	67.33	85.6	92.89	85.1	112.3	83.9
32	51.11	89.1	69.91	88.9	96.24	87.2	116.4	86.9
128	53.96	94.1	73.92	94.0	101.5	91.9	122.9	91.8
512	55.55	96.9	77.52	97.0	106.3	96.6	128.6	96.0
1024	56.08	97.8	77.62	98.7	107.2	97.1	130.3	97.3
2048	57.34	100.0	78.64	100.0	110.4	100.0	133.9	100.0

Table III.—Temperature Coefficients.

	0° to 11°.2.		11°.2 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.24	3.00	1.49	2.69	1.59	2.10
8	1.51	3.41	1.75	2.72	1.75	1.98
16	1.62	3.39	1.85	2.75	1.94	2.09
32	1.68	3.29	1.91	2.73	2.02	2.10
128	1.79	3.32	2.00	2.70	2.14	2.11
512	1.90	3.42	2.08	2.69	2.23	2.10
1024	1.92	3.42	2.15	2.77	2.31	2.15
2048	....	....	2.28	2.90	2.35	2.13

Lithium Bromide.
Table IV.—*Molecular Conductivity.*

V.	0°.	9°.3.	25°.	35°.
2	44.83	55.94	78.52	96.02
8	49.84	63.42	89.78	109.5
16	51.51	66.75	95.03	114.9
32	53.10	68.77	98.66	119.5
128	56.57	73.70	106.7	128.6
512	57.44	75.06	108.2	130.6
1024	57.97	75.99	109.9	133.3
2048	61.05	80.68	114.8	138.3

Table V.—*Percentage Dissociation.*

V.	0°.	9°.3.	25°.	35°.
2	73.4	69.3	68.4	69.4
8	81.6	78.6	78.2	79.2
16	84.4	82.7	82.8	83.1
32	87.0 ·	85.2	85.9	86.4
128	92.7	91.4	92.9	93.0
512	94.1	93.0	94.3	94.4
1024	95.0	94.2	95.7	96.4
2048	100.0	100.0	100.0	100.0

Table VI.—*Temperature Coefficients.*

V.	0° to 9°.3.		9°.3 to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.19	2.66	1.43	2.56	1.75	2.23
8	1.46	2.93	1.67	2.63	1.97	2.19
16	1.63	3.16	1.80	2.70	1.99	2.09
32	1.68	3.16	1.90	2.91	2.08	2.11
128	1.84	3.25	2.10	2.85	2.19	2.05
512	1.89	3.29	2.11	2.81	2.24	2.07
1024	1.94	3.35	2.16	2.84	2.34	2.13
2048	2.33	3.82	2.17	2.68	2.35	2.05

Lithium Nitrate.

Table VII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	38.65	52.28	70.56	82.20
8	43.83	57.79	79.71	96.99
16	45.96	60.32	84.16	100.9
32	47.27	62.51	87.39	105.1
128	51.05	66.88	93.29	112.2
512	51.53	68.07	96.03	115.6
1024	52.00	69.47	98.01	117.8
2048	52.40	70.01	100.03	121.0

Table VIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	73.8	74.7	70.4	67.9
8	83.6	82.5	79.5	80.2
16	87.7	86.2	83.9	83.4
32	90.2	89.3	87.1	86.9
128	97.4	95.5	93.0	92.7
512	98.3	97.2	95.7	95.5
1024	99.2	99.2	97.7	97.4
2048	100.0	100.0	100.0	100.0

Table IX.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25°. to 35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.26	3.26	1.35	2.58	1.64	2.32
8	1.40	3.19	1.46	2.53	1.67	2.09
16	1.44	3.13	1.59	2.64	1.70	2.02
32	1.52	3.22	1.66	2.67	1.77	2.03
128	1.58	3.10	1.76	2.63	1.89	2.03
512	1.65	3.20	1.86	2.73	1.96	2.04
1024	1.75	3.36	1.90	2.73	1.98	2.02
2048	1.76	3.36	2.02	2.89	2.07	2.06

Lithium Sulphate.

Table X.—*Molecular Conductivity.*

V.	0°.	9°.6.	25°.	35°.
2	47.08	61.97	89.59	107.5
8	66.74	88.18	128.4	154.9
16	75.50	100.2	144.5	175.3
32	82.15	109.5	159.3	194.0
128	96.81	129.0	188.5	230.3
512	104.6	139.1	202.8	248.3
1024	108.1	143.8	211.4	258.8
2048	111.8	148.0	219.5	268.0

Table XI.—*Percentage Dissociation.*

V.	0°.	9°.6.	25°.	35°.
2	42.1	41.9	40.8	40.1
8	59.7	59.6	58.5	57.8
16	67.5	67.7	65.8	65.4
32	73.5	74.0	72.6	72.4
128	86.6	87.2	85.9	85.9
512	93.6	94.0	92.4	92.7
1024	96.7	97.2	96.3	96.6
2048	100.0	100.0	100.0	100.0

Table XII.—*Temperature Coefficients.*

	0° to 9°.6.		9°.6 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.55	3.29	1.68	2.71	1.79	2.00
8	2.23	3.34	2.25	2.55	2.65	2.06
16	2.57	3.40	2.88	2.87	3.08	2.13
32	2.85	3.47	3.23	2.96	3.47	2.18
128	3.35	3.46	3.86	2.99	4.18	2.22
512	3.59	3.43	4.14	2.98	4.55	2.25
1024	3.72	3.41	4.39	3.05	4.74	2.24
2048	3.77	3.37	4.64	3.13	4.85	2.21

Sodium Nitrate.

Table XIII.—Molecular Conductivity and Percentage Dissociation.

V.	0°.		25°.		35°.	
	$\mu v.$	$\alpha.$	$\mu v.$	$\alpha.$	$\mu v.$	$\alpha.$
2	43.34	72.3	78.1	67.0	91.7	65.0
8	50.27	83.9	90.9	77.9	111.3	78.9
16	52.57	86.1	97.5	83.6	117.5	83.3
32	55.38	92.4	101.3	86.9	122.5	86.9
128	59.28	98.9	107.7	92.3	128.9	91.4
512	59.34	99.0	111.3	95.5	134.8	95.6
1024	59.39	99.8	114.0	97.8	138.5	98.2
2048	59.93	100.0	116.6	100.0	141.0	100.0

Table XIV.—Temperature Coefficients.

V.	0° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.39	3.21	1.36	1.74
8	1.62	3.22	2.04	2.24
16	1.79	3.41	2.00	2.44
32	1.83	3.30	2.12	2.05
128	1.94	3.27	2.12	1.94
512	2.08	3.51	2.35	2.11
1024	2.18	3.68	2.45	2.15
2048	2.27	3.79	2.44	2.09

Disodium Phosphate.

Table XV.—*Molecular Conductivity and Percentage Dissociation.*

	0°.		25°.		30°.	
V.	*μv.*	*α.*	*μv.*	*α.*	*μv.*	*α.*
16	67.3	68.8	133.4	72.5	148.6	72.1
32	75.0	81.5	147.8	80.3	164.5	79.8
128	88.4	96.1	168.6	91.5	188.1	91.2
512	91.7	99.7	182.3	99.1	203.8	98.8
1024	91.9	99.9	183.7	99.8	205.2	99.5
2048	92.0	100.0	184.0	100.0	206.2	100.0

Table XVI.—*Temperature Coefficients.*

	0° to 25°.		25° to 30°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	2.64	4.17	3.04	2.28
32	2.91	3.88	3.34	2.26
128	3.21	3.63	3.90	2.32
512	3.62	3.95	4.30	2.35
1024	3.67	3.99	4.30	2.34
2048	3.68	4.00	4.44	2.41

Potassium Sulphocyanate.

Table XVII.—Molecular Conductivity.

V.	0°.	13°.5.	25°.	30°.
2	57.75	79.47	100.0	110.2
8	62.48	87.87	110.9	121.9
16	64.26	90.81	115.4	126.8
32	65.99	93.39	118.7	130.8
128	70.70	100.1	127.3	139.4
512	71.28	101.2	129.8	142.3
1024	72.25	102.6	131.5	144.3
2048	72.86	103.0	133.7	147.3

Table XVIII.—Percentage Dissociation.

V.	0°.	13°.5.	25°.	30°.
2	79.3	77.2	74.8	74.8
8	85.8	85.3	83.0	82.8
16	88.2	88.2	86.3	86.1
32	90.6	90.7	88.8	88.8
128	97.0	97.2	95.2	94.6
512	97.8	98.3	97.1	96.6
1024	99.2	99.6	98.4	98.0
2048	100.0	100.0	100.0	100.0

Table XIX.—Temperature Coefficients.

	0° to 13°.5.		13°.5 to 25°.		25° to 30°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.31	2.27	1.78	2.24	2.04	2.04
8	1.88	3.00	2.00	2.28	2.20	1.98
16	1.97	3.07	2.14	2.36	2.28	1.98
32	2.04	3.09	2.18	2.33	2.41	2.03
128	2.18	3.08	2.38	2.38	2.42	1.90
512	2.23	3.13	2.46	2.43	2.50	1.93
1024	2.26	3.13	2.49	2.43	2.56	1.95
2048	2.24	3.07	2.60	2.52	2.72	2.03

Potassium Chromate.

Table XX.—*Molecular Conductivity.*

V.	0°.	12°.2.	25°.	35°.
2	96.50	128.1	165.7	197.5
8	111.3	151.9	196.0	235.4
16	117.8	163.5	213.5	256.0
32	124.6	173.7	227.2	272.0
128	140.1	191.1	252.9	303.0
512	147.1	205.5	272.0	327.8
1024	150.1	209.2	276.2	330.2
2048	151.4	211.5	279.9	334.3

Table XXI.—*Percentage Dissociation.*

V.	0°.	12°.2.	25°.	35°.
2	63.7	60.6	59.2	59.6
8	73.5	71.8	70.0	70.4
16	77.8	77.3	76.3	76.6
32	82.3	82.1	81.2	81.4
128	92.5	90.4	90.4	90.6
512	97.2	97.2	97.2	98.1
1024	99.1	98.9	98.7	98.8
2048	100.0	100.0	100.0	100.0

Table XXII.—*Temperature Coefficients.*

	0° to 12°.2.		12°.2 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent
2	2.59	2.68	2.93	2.29	3.18	1.92
8	3.35	3.00	3.45	2.27	3.94	2.01
16	3.74	3.17	3.90	2.39	4.25	1.99
32	4.04	3.24	4.17	2.40	4.48	1.97
128	4.18	2.98	4.82	2.52	5.01	1.98
512	4.78	3.24	5.19	2.53	5.44	2.00
1024	4.84	3.22	5.23	2.50	5.40	1.96
2048	4.93	3.26	5.34	2.52	5.44	1.94

Potassium Dichromate.
Table XXIII.—Molecular Conductivity.

V.	0°.	12°.6.	25°.	35°.
8	109.1	150.8	195.5	234.0
16	116.6	161.5	209.3	248.8
32	122.6	168.8	219.4	260.9
128	129.9	178.8	231.5	277.3
512	133.0	182.5	237.3	281.2
1024	133.6	185.7	240.6	287.9
2048	136.8	188.8	245.5	293.6

Table XXIV.—Percentage Dissociation.

V.	0°.	12°.6.	25°.	35°.
8	79.8	79.9	79.6	79.6
16	85.2	85.5	85.3	84.7
32	89.6	89.4	89.4	88.9
128	95.0	94.7	94.3	94.4
512	97.2	96.7	96.7	95.8
1024	97.7	98.4	98.0	98.1
2048	100.0	100.0	100.0	100.0

Table XXV.—Temperature Coefficients.

V.	0° to 12°.6.		12°.6 to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.31	3.03	3.60	2.19	3.85	1.97
16	3.56	3.05	3.85	2.38	3.95	1.89
32	3.66	2.98	4.08	2.42	4.15	1.89
128	3.88	2.99	4.25	2.38	4.39	1.90
512	3.93	2.95	4.42	2.42	4.45	1.88
1024	4.13	3.09	4.43	2.39	4.73	1.97
2048	4.13	3.02	4.57	2.42	4.81	1.96

Calcium Nitrate.

Table XXVI.—*Molecular Conductivity.*

V.	0°.	9°.7.	25°.	35°.
2	65.84	85.83	121.0	145.0
8	85.50	112.8	157.3	188.2
16	94.95	123.9	174.2	209.8
32	102.3	133.5	187.7	225.6
128	114.5	151.0	212.0	255.4
512	122.6	160.6	226.7	274.2
1024	125.7	164.2	235.0	282.9
2048	130.0	171.4	242.7	292.4

Table XXVII.—*Percentage Dissociation.*

V.	0°.	9°.7.	25°.	35°.
2	50.7	50.1	49.9	49.6
8	65.8	65.8	64.8	64.4
16	73.0	72.3	71.8	71.8
32	78.7	77.9	77.3	77.2
128	88.1	88.1	87.4	87.4
512	94.3	93.7	93.4	93.8
1024	96.7	95.8	96.8	96.8
2048	100.0	100.0	100.0	100.0

Table XXVIII.—*Temperature Coefficients.*

	0° to 9°.7.		9°.7 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.04	3.10	2.31	2.69	2.40	1.98
8	2.81	3.29	2.91	2.58	3.09	1.96
16	2.98	3.14	3.29	2.82	3.56	2.04
32	3.22	3.15	3.54	2.62	3.79	2.02
128	3.76	3.28	3.99	2.64	4.34	2.05
512	3.92	3.19	4.32	2.69	4.75	2.10
1024	4.01	3.19	4.60	2.80	4.79	2.04
2048	4.31	3.32	4.64	2.71	4.97	2.05

Strontium Chloride.

Table XXIX.—*Molecular Conductivity.*

V.	0°.	9°.9.	25°.	35°.
2	81.36	106.2	141.5	172.0
8	92.97	124.3	173.7	207.4
16	101.1	134.5	187.7	225.9
32	106.3	141.5	198.4	238.7
128	118.5	157.6	225.0	271.6
512	125.0	166.1	236.7	285.4
1024	129.1	171.4	242.8	294.1
2048	133.9	176.1	248.7	300.3
4096	133.3	176.0	248.6	(303.9)

Table XXX.—*Percentage Dissociation.*

V.	0°.	9°.9.	25°.	35°.
2	60.8	60.3	56.9	57.3
8	69.5	70.6	69.8	69.1
16	75.5	76.4	75.5	75.2
32	79.4	80.4	79.8	79.5
128	88.5	89.5	90.5	90.5
512	93.4	94.3	95.2	95.0
1024	96.4	97.3	97.6	97.9
2048	100.0	100.0	100.0	100.0
4096	100.0	100.0	100.0	100.0

Table XXXI.—*Temperature Coefficients.*

V.	0° to 9°.9.		9°.9 to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.51	3.09	2.34	2.20	3.05	2.16
8	3.16	3.39	3.27	2.63	3.37	1.94
16	3.38	3.34	3.52	2.62	3.82	2.03
32	3.56	3.35	3.90	2.76	4.03	2.03
128	3.96	3.34	4.46	2.83	4.66	2.07
512	4.15	3.32	4.67	2.81	4.87	2.06
1024	4.27	3.31	4.73	2.76	5.13	2.11
2048	4.27	3.22	4.81	2.73	5.16	2.07
4096	4.31	3.23	4.81	2.73	5.31	2.14

Strontium Nitrate.
Table XXXII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	63.24	81.25	112.4	135.4
8	84.33	112.8	154.1	181.7
16	93.33	124.8	171.4	205.7
32	100.7	133.3	185.3	223.5
128	114.8	151.4	211.2	254.0
512	122.5	161.6	227.1	273.5
1024	126.9	167.0	233.7	282.3
2048	131.3	171.9	238.6	287.5

Table XXXIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	48.2	47.3	47.1	47.1
8	64.2	65.5	64.6	63.2
16	71.1	72.6	71.8	71.5
32	77.7	77.5	77.7	77.7
128	87.4	88.1	88.5	88.4
512	93.3	94.0	95.2	95.1
1024	96.7	97.2	97.9	98.2
2048	100.0	100.0	100.0	100.0

Table XXXIV.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.80	2.85	2.07	2.55	2.30	2.05
8	2.85	3.38	2.75	2.44	2.76	1.79
16	3.14	3.36	3.11	2.49	3.43	2.00
32	3.26	3.24	3.47	2.60	3.82	2.06
128	3.66	3.19	3.99	2.63	4.28	2.03
512	3.91	3.19	4.37	2.70	4.64	2.04
1024	4.01	3.16	4.45	2.66	4.86	2.08
2048	4.06	3.10	4.45	2.59	4.89	2.05

Strontium Formate.
Table XXXV.—Molecular Conductivity.

V.	0°.	15°.5.	25°.	35°.
2	48.82	73.05	89.25	107.9
8	69.86	105.2	130.0	157.9
16	77.61	119.1	147.9	178.6
32	85.69	129.9	160.7	195.8
128	99.57	147.9	184.0	225.0
512	105.0	153.5	193.4	237.7
1024	109.0	168.6	209.0	254.1
2048	111.8	172.2	212.5	258.1

Table XXXVI.—Percentage Dissociation.

V.	0°.	15°.5.	25°.	35°.
2	43.7	42.4	42.0	41.8
8	62.5	61.1	61.2	61.1
16	69.4	69.0	69.6	69.2
32	76.6	75.4	75.6	75.9
128	89.1	85.9	86.6	87.2
512	93.9	89.2	91.0	92.1
1024	97.5	97.9	98.3	98.5
2048	100.0	100.0	100.0	100.0

Table XXXVII.—Temperature Coefficients.

V.	0° to 15°.5.		15°.5 to 25°.		25° to 35°.	
	Cond. units	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.56	3.20	1.70	2.32	1.87	2.09
8	2.27	3.25	2.61	2.48	2.77	2.13
16	2.67	3.44	3.03	2.54	3.07	2.08
32	2.85	3.32	3.24	2.49	3.51	2.18
128	3.11	3.13	3.80	2.57	4.10	2.23
512	3.13	2.98	4.12	2.68	4.43	2.29
1024	3.84	3.52	4.25	2.52	4.49	2.24
2048	3.91	3.49	4.24	2.46	4.56	2.14

Barium Bromide.

Table XXXVIII.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	91.81	119.3	158.6	188.1
8	103.4	137.0	187.4	224.0
16	109.3	144.8	198.9	238.8
32	114.4	151.0	209.4	251.4
128	123.6	163.7	228.5	274.4
512	131.8	175.5	246.8	298.2
1024	133.8	177.2	249.9	301.6
2048	134.2	178.7	252.6	305.7

Table XXXIX.—*Percentage Dissociation.*

V.	0°.	10°.	25°.	35°.
2	68.4	66.8	62.8	61.5
8	77.1	76.7	74.2	73.3
16	81.5	81.0	78.7	78.1
32	85.3	84.5	82.9	82.2
128	92.1	91.6	90.5	89.8
512	98.2	98.2	97.7	97.6
1024	99.7	99.2	98.9	98.7
2048	100.0	100.0	100.0	100.0

Table XL.—*Temperature Coefficients.*

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.74	2.98	2.62	2.20	2.95	1.86
8	3.36	3.25	3.36	2.45	3.66	1.95
16	3.55	3.25	3.60	2.49	3.99	2.01
32	3.66	3.20	3.89	2.58	4.20	2.01
128	4.01	3.24	4.32	2.64	4.59	2.01
512	4.37	3.32	4.75	2.71	5.14	2.08
1024	4.34	3.24	4.85	2.74	5.18	2.07
2048	4.45	3.32	4.93	2.76	5.24	2.07

Barium Nitrate.

Table XLI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
8	76.37	103.0	146.4	177.3
16	88.29	117.6	165.2	200.1
32	97.62	129.8	183.2	219.8
128	114.4	150.8	210.0	251.8
512	124.3	163.8	229.2	275.2
1024	127.4	167.8	234.2	281.6
2048	131.4	171.6	239.8	288.8

Table XLII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
8	58.1	60.0	61.1	61.4
16	67.2	68.5	68.9	69.3
32	74.3	75.6	76.4	76.1
128	87.1	87.9	87.6	87.2
512	94.6	95.5	95.6	95.3
1024	97.0	97.8	97.7	97.5
2048	100.0	100.0	100.0	100.0

Table XLIII.—Temperature Coefficients.

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond units.	Per cent.
8	2.66	3.48	2.89	2.81	3.09	2.11
16	2.93	3.32	3.17	2.70	3.49	2.11
32	3.22	3.30	3.56	2.74	3.66	2.00
128	3.64	3.18	3.95	2.62	4.18	1.99
512	3.95	3.18	4.36	2.66	4.60	2.01
1024	4.04	3.17	4.43	2.64	4.74	2.02
2048	4.02	3.06	4.55	2.65	4.90	2.04

Barium Formate.

Table XLIV.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	51.67	67.74	93.97	112.1
8	72.22	95.34	133.4	159.2
16	77.72	102.7	144.6	173.8
32	85.56	114.3	160.6	193.1
128	86.20	114.3	162.4	197.4
512	102.2	133.6	182.0	215.2
1024	103.0	135.0	184.0	226.2
2048	111.8	149.4	210.0	257.6

Table XLV.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	46.2	45.3	44.8	43.5
8	64.6	63.8	63.5	61.8
16	69.5	68.7	68.9	69.0
32	76.5	76.5	76.5	75.0
128	77.1	76.5	77.3	76.6
512	91.4	89.4	86.7	83.5
1024	92.1	90.3	87.7	87.8
2048	100.0	100.0	100.0	100.0

Table XLVI.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.60	3.10	1.75	2.58	1.81	1.93
8	2.31	3.20	2.54	2.66	2.58	1.93
16	2.49	3.20	2.79	2.72	2.92	2.02
32	2.87	3.35	3.09	2.70	3.25	2.02
128	2.81	3.26	3.27	2.86	3.50	2.16
512	3.15	3.08	3.23	2.41	3.32	1.82
1024	3.20	3.10	3.33	2.46	4.22	2.29
2048	3.76	3.36	4.04	2.70	4.76	2.27

Barium Acetate.

Table XLVII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	40.16	53.25	76.18	89.95
8	59.05	79.46	113.3	136.0
16	65.68	87.10	124.3	149.3
32	72.93	97.58	139.5	168.6
128	78.15	104.5	149.0	181.2
512	90.75	123.1	176.9	215.8
1024	92.63	124.7	180.5	219.8
2048	95.96	129.3	186.3	226.7

Table XLVIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	41.9	41.2	40.9	39.7
8	63.0	61.5	60.8	60.0
16	68.4	67.4	66.7	66.0
32	76.0	75.5	74.9	74.4
128	81.4	80.8	80.0	79.9
512	94.6	95.2	95.0	95.2
1024	96.5	96.4	96.9	97.0
2048	100.0	100.0	100.0	100.0

Table XLIX.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units	Per cent.	Cond. units.	Per cent.
2	1.30	3.24	1.52	2.85	1.37	1.80
8	2.04	3.45	2.26	2.84	2.27	2.00
16	2.14	3.26	2.48	2.85	2.52	2.03
32	2.46	3.38	2.79	2.86	2.91	2.09
128	3.63	3.37	2.97	2.84	3.22	2.16
512	3.23	3.06	3.59	2.91	3.89	2.20
1024	3.20	3.45	3.72	2.98	3.93	2.18
2048	3.33	3.47	3.80	2.93	4.04	2.17

Magnesium Sulphate.

Table L.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	32.12	43.14	60.57	72.68
8	45.70	60.90	85.62	102.4
16	50.95	68.14	96.50	115.0
32	59.57	79.73	112.4	135.3
128	71.17	95.38	135.9	164.4
512	95.57	128.3	183.3	221.9
1024	102.7	138.4	198.3	240.9
2048	111.1	148.5	215.2	261.0

Table LI.—*Percentage Dissociation.*

V.	0°.	10°.	25°.	35°.
2	28.9	29.1	28.2	27.8
8	41.1	41.0	39.8	39.2
16	45.9	45.9	44.8	44.1
32	53.6	53.7	52.2	51.8
128	64.1	64.2	63.2	63.0
512	86.0	84.4	85.2	85.0
1024	92.4	93.2	92.3	92.3
2048	100.0	100.0	100.0	100.0

Table LII.—*Temperature Coefficients.*

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.10	3.42	1.16	2.69	1.21	2.00
8	1.52	3.33	1.65	2.71	1.67	1.95
16	1.71	3.36	1.89	2.77	1.85	1.92
32	2.01	3.37	2.18	2.73	2.29	2.04
128	2.42	3.40	2.75	2.88	2.85	2.10
512	3.27	3.42	3.73	2.91	3.86	2.11
1024	3.57	3.48	3.99	2.88	4.26	2.15
2048	3.74	3.37	4.45	2.99	4.58	2.22

Cupric Bromide.

Table LIII.—Molecular Conductivity.

V.	0°.	13°.3.	25°.	35°.
2	75.27	103.9	135.3	156.1
8	91.31	131.0	169.6	203.8
16	99.30	141.4	183.0	220.3
32	105.0	149.8	194.3	234.1
128	118.2	169.0	220.0	266.0
512	122.2	177.3	230.8	278.4
1024	125.4	181.2	236.6	285.9
2048	131.4	187.5	242.7	295.0
4096	...	...	248.8	300.2
8192	...	...	274.8	325.1

Table LIV.—Percentage Dissociation.

V.	0°.	13°.3.	25°.	35°.
2	57.3	55.4	55.7	52.9
8	69.5	69.9	69.9	69.1
16	75.6	75.4	75.4	74.7
32	79.9	79.9	80.1	79.3
128	90.0	90.1	90.6	90.2
512	93.0	94.6	95.1	94.4
1024	95.4	96.6	97.5	96.9
2048	100.0	100.0	100.0	100.0

Table LV.—Temperature Coefficients.

V.	0° to 13°.3.		13°.3 to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.16	2.87	2.68	2.58	2.08	1.54
8	2.99	3.27	3.30	2.51	3.42	2.02
16	3.17	3.19	3.50	2.48	3.73	2.04
32	3.37	3.21	3.75	2.50	3.98	2.04
128	3.82	3.23	4.35	2.57	4.60	2.09
512	4.14	3.38	4.37	2.57	4.76	2.06
1024	4.19	3.34	4.73	2.61	4.93	2.08
2048	4.22	3.21	4.72	2.52	5.23	2.15
4096	..	..	..	..	5.14	..
8192	..	..	..	..	5.03	..

Chromium Chloride.

Table LVI.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
8	116.3	153.7	216.9	261.7
16	128.7	171.1	243.0	294.5
32	137.5	184.2	262.9	319.9
128	152.6	204.5	297.0	365.3
512	190.6	260.8	384.0	475.4
1024	204.9	280.5	420.5	522.8
2048	214.6	294.3	441.7	553.4

Table LVII.—*Percentage Dissociation.*

V.	0°.	10°.	25°.	35°.
8	54.2	52.2	49.1	47.3
16	60.0	58.1	55.0	53.2
32	64.1	62.6	59.5	57.8
128	71.1	69.5	67.2	66.0
512	88.8	88.6	86.9	85.9
1024	95.5	95.3	95.2	94.5
2048	100.0	100.0	100.0	100.0

Table LVIII.—*Temperature Coefficients.*

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.74	3.30	4.21	2.74	4.48	2.07
16	4.24	3.29	4.79	2.80	5.15	2.12
32	4.67	3.40	5.25	2.85	5.70	2.17
128	5.19	3.40	6.17	3.35	6.83	2.29
512	7.02	3.68	8.21	3.15	9.14	2.30
1024	7.56	3.69	9.33	3.33	10.23	2.43
2048	7.97	3.71	9.83	3.34	11.17	2.53

Chromium Nitrate.
Table LIX.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	87.17	112.1	154.7	183.6
8	117.6	153.1	214.0	256.5
16	129.7	169.7	238.8	287.4
32	138.5	181.9	258.1	312.6
128	149.0	198.9	286.2	350.7
512	188.7	253.0	370.2	459.4
1024	203.0	274.0	412.9	511.8
2048	210.4	295.3	438.0	550.9

Table LX.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	41.4	38.0	35.3	33.3
8	55.9	51.9	48.9	46.6
16	61.6	57.5	54.5	52.2
32	65.8	61.8	58.9	56.8
128	70.8	67.4	65.3	63.7
512	89.7	85.7	84.5	83.6
1024	96.5	92.8	94.3	93.4
2048	100.0	100.0	100.0	100.0

Table LXI.—Temperature Coefficients.

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.49	2.86	2.84	2.53	2.89	1.87
8	3.55	3.02	4.06	2.65	4.25	1.99
16	4.00	3.08	4.61	2.72	4.86	2.04
32	4.34	3.13	5.08	2.79	5.45	2.11
128	4.99	3.35	5.82	2.93	6.45	2.25
512	6.43	3.41	7.81	3.09	8.92	2.41
1024	7.10	3.50	9.26	3.38	9.89	2.40
2048	8.49	4.04	9.51	3.22	11.29	2.58

Ferric Chloride.
Table LXII.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	80.50	104.6	143.6	169.9
8	127.2	168.5	238.1	285.4
16	143.4	190.7	274.6	332.7
32	166.7	226.0	328.3	400.4
128	198.9	274.0	401.9	508.9
512	351.2	563.1	707.2	945.0
1024	486.3	688.4	892.4	1130.3
2048	609.7	799.9	1028.2	1235.6

Table LXIII.—*Temperature Coefficients.*

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.41	2.99	2.60	2.49	2.65	1.85
8	4.13	3.25	4.64	2.75	4.73	1.99
16	4.73	3.30	5.59	2.93	5.81	2.12
32	5.93	3.56	6.82	3.02	7.21	2.20
128	7.51	3.78	8.53	3.11	10.70	2.66
512	21.1	6.01	9.61	1.71	23.78	3.36
1024	20.2	4.15	13.66	1.98	23.60	2.64
2048	19.0	3.12	12.27	1.50	24.16	2.35

Ferric Nitrate.

Table LXIV.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	97.68	128.1	181.6	220.7
8	138.2	185.7	266.5	328.2
16	150.7	202.7	295.3	364.3
32	171.4	233.7	342.6	422.6
128	199.5	271.7	399.4	491.4
512	371.3	408.7	705.7	927.0
1024	490.9	571.4	877.7	1116.5
2048	585.2	693.5	961.6	1183.0

Table LXV.—*Temperature Coefficients.*

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	3.04	3.12	3.57	2.79	3.91	2.15
8	4.75	3.44	5.39	2.90	6.17	2.32
16	5.20	3.44	6.17	3.04	6.90	2.34
32	6.23	3.63	7.26	3.11	8.00	2.34
128	7.22	3.62	8.50	3.13	9.20	2.30
512	3.74	1.01	19.80	4.84	22.13	3.14
1024	8.05	1.64	20.42	3.57	23.88	2.72
2048	10.83	1.85	18.61	2.68	22.14	2.30

Nickel Sulphate.

Table LXVI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	28.77	38.37	54.58	64.38
8	40.38	54.42	77.06	90.95
16	47.78	64.00	90.44	106.9
32	54.78	73.23	103.5	123.0
128	73.95	99.92	140.3	168.4
512	93.12	124.7	177.5	213.5
1024	100.4	134.8	193.8	234.6
2048	108.3	145.5	208.7	253.9

Table LXVII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	26.6	25.8	26.2	25.4
8	37.5	37.4	36.9	35.8
16	44.1	44.0	43.3	42.1
32	50.6	50.3	49.6	48.5
128	68.3	68.7	67.2	66.3
512	86.0	85.7	85.1	84.1
1024	92.7	92.6	92.9	92.4
2048	100.0	100.0	100.0	100.0

Table LXVIII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.96	3.34	1.08	2.81	0.98	1.80
8	1.38	3.40	1.50	2.75	1.39	1.80
16	1.62	3.39	1.76	2.75	1.64	1.81
32	1.84	3.36	2.01	2.74	1.95	1.88
128	2.59	3.50	2.69	2.69	2.81	2.00
512	3.16	3.39	3.52	2.82	3.60	2.03
1024	3.44	3.43	3.93	2.91	4.08	2.11
2048	3.72	3.43	4.21	2.89	4.52	2.17

Nickel Acetate.

Table LXIX.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	20.11	27.24	39.22	47.46
8	38.95	52.07	74.10	89.29
16	47.81	64.03	91.60	110.2
32	54.11	73.82	105.8	128.1
128	69.22	92.82	134.6	164.0
512	76.66	103.5	150.7	184.7
1024	78.65	105.9	153.9	189.1
2048	82.24	110.9	160.6	196.6

Table LXX.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	24.5	24.6	24.4	24.1
8	47.4	47.0	45.1	45.4
16	56.8	57.7	57.0	56.1
32	65.8	66.6	65.9	65.2
128	84.2	83.7	83.8	83.4
512	93.2	93.3	93.8	93.9
1024	95.6	95.5	95.8	96.2
2048	100.0	100.0	100.0	100.0

Table LXXI.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.71	3.53	0.79	2.90	0.82	2.09
8	1.31	3.39	1.47	2.82	1.51	2.04
16	1.62	3.39	1.84	2.87	1.86	2.03
32	1.97	3.64	2.13	2.89	2.23	2.11
128	2.36	3.41	2.78	3.00	2.94	2.18
512	2.68	3.50	3.14	3.03	3.40	2.26
1024	2.72	3.46	3.20	3.02	3.52	2.29
2048	2.86	3.48	3.31	2.98	3.60	2.24

Cobalt Sulphate.

Table LXXII.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	29.47	39.22	55.10	65.57
8	42.06	56.00	78.37	93.14
16	49.26	65.61	91.97	109.4
32	56.26	75.04	105.4	125.8
128	75.89	101.5	143.4	172.1
512	94.88	126.9	180.2	218.1
1024	101.9	137.6	196.9	239.2
2048	110.9	148.4	214.1	259.2

Table LXXIII.—*Percentage Dissociation.*

V.	0°.	10°.	25°.	35°.
2	26.6	26.4	25.7	25.3
8	37.9	37.7	36.6	35.9
16	44.4	44.2	43.0	42.2
32	50.7	50.6	49.2	48.5
128	68.4	68.4	67.0	66.4
512	85.6	85.5	84.2	84.2
1024	91.9	92.7	92.0	92.3
2048	100.0	100.0	100.0	100.0

Table LXXIV.—*Temperature Coefficients.*

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.97	3.29	1.06	2.70	1.04	1.89
8	1.39	3.30	1.49	2.66	1.47	1.88
16	1.63	3.31	1.76	2.68	1.74	1.89
32	1.88	3.34	2.02	2.69	2.04	1.94
128	2.56	3.37	2.79	2.75	2.87	2.00
512	3.21	3.38	3.55	2.79	3.79	2.10
1024	3.57	3.50	3.95	2.87	4.23	2.15
2048	3.75	3.38	4.38	2.95	4.51	2.11

Cobalt Acetate.
Table LXXV.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	22.20	29.79	42.55	51.02
8	41.31	55.27	78.37	94.00
16	50.07	67.20	95.68	114.9
32	56.92	76.66	109.8	132.1
128	71.25	95.67	136.8	166.3
512	78.29	106.0	153.6	188.1
1024	78.88	107.1	155.3	189.8
2048	82.71	113.2	163.7	199.3

Table LXXVI.—*Percentage Dissociation.*

V.	0°.	10°.	25°.	35°.
2	26.8	26.3	26.0	25.6
8	50.0	48.8	47.9	46.1
16	60.5	59.4	58.5	57.7
32	68.8	67.7	67.1	66.3
128	86.1	84.5	83.6	83.4
512	94.7	93.6	93.8	94.4
1024	95.4	94.6	94.9	95.2
2048	100.0	100.0	100.0	100.0

Table LXXVII.—*Temperature Coefficients.*

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.75	3.37	0.85	2.85	0.87	2.04
8	1.39	3.36	1.54	2.79	1.56	1.99
16	1.71	3.42	1.90	2.83	1.92	2.01
32	1.97	3.46	2.21	2.88	2.23	2.03
128	2.44	3.42	2.74	2.86	2.95	2.16
512	2.77	3.54	3.15	2.97	3.45	2.25
1024	2.82	3.58	3.21	2.99	3.45	2.22
2048	3.05	3.69	3.37	2.98	3.56	2.17

Lead Nitrate.

Table LXXVIII.—*Molecular Conductivity.*

V.	0°.	10°.	25°.	35°.
2	46.30	63.55	92.68	113.0
8	71.12	97.32	139.8	169.5
16	84.43	103.3	161.5	195.6
32	93.85	128.3	181.5	118.8
128	115.1	153.1	214.0	256.7
512	129.1	171.9	238.3	287.1
1024	133.6	178.1	247.4	297.5
2048	135.1	178.7	247.2	299.0

Table LXXIX.—*Percentage Dissociation.*

V.	0°.	10°.	25°.	35°.
2	34.3	35.6	37.5	37.8
8	52.6	54.5	55.3	56.7
16	62.5	63.4	65.3	65.4
32	69.5	71.8	73.4	73.2
128	85.2	85.7	86.6	85.9
512	95.6	96.2	96.4	96.0
1024	98.9	99.7	100.0	99.5
2048	100.0	100.0	100.0	100.0

Table LXXX.—*Temperature Coefficients.*

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.72	3.71	1.94	3.05	2.03	2.19
8	2.62	3.68	2.83	2.91	2.97	2.12
16	2.88	3.41	3.21	2.83	3.41	2.11
32	3.44	3.67	3.55	2.77	3.73	2.05
128	3.80	3.30	4.06	2.65	4.27	2.00
512	4.28	3.32	4.43	2.58	4.88	2.05
1024	4.45	3.33	4.62	2.59	5.01	2.03
2048	4.36	3.23	4.57	2.55	5.18	2.10

Trichloracetic Acid.
Table LXXXI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	161.3	198.8	250.1	279.7
8	194.0	241.6	305.3	346.5
16	204.6	252.6	320.6	363.8
32	210.5	260.2	332.4	377.8
128	215.5	268.4	343.5	391.3
512	221.2	275.5	350.7	400.2
1024	220.3	272.6	350.4	399.3
2048	217.4	272.9	347.0	396.7

Table LXXXII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	72.9	72.2	71.3	69.9
8	87.7	87.7	87.1	86.6
16	92.5	91.7	91.4	90.9
32	95.5	94.5	94.8	94.4
128	97.4	97.4	97.9	97.8
512	100.0	100.0	100.0	100.0
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Table LXXXIII.—Temperature Coefficients.

V.	0° to 10°.		10° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	3.75	2.32	3.42	1.72	2.96	1.18
8	4.76	2.45	4.25	1.76	4.12	1.35
16	4.80	2.35	4.53	1.79	4.32	1.35
32	4.97	2.36	4.81	1.85	4.54	1.37
128	5.29	2.45	5.00	1.86	4.78	1.39
512	5.43	2.45	5.01	1.82	4.95	1.41
1024	5.23	2.37	5.24	1.92	4.89	1.40
2048	5.55	2.55	4.94	1.81	4.97	1.43

Racemic Acid.

Table LXXXIV.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
2	8.77	12.60	15.19	17.54
8	17.87	25.70	30.89	35.65
16	24.72	35.64	42.89	49.46
32	34.04	49.17	59.02	68.18
128	62.32	90.59	108.4	124.8
512	109.0	155.0	184.4	212.5
1024	134.7	190.0	220.6	247.3
2048	169.5	238.3	290.9	336.7

Table LXXXV.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
2	4.23	4.32	4.27	4.26
8	6.61	8.80	8.68	8.65
16	11.9	12.2	12.1	12.0
32	16.4	16.8	· 16.6	16.6
128	30.2	31.0	30.5	30.3
512	52.5	53.1	51.8	51.6
1024	64.9	65.1	62.0	60.0
2048	81.7	81.6	81.7	81.7

Table LXXXVI.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.26	2.91	0.26	2.06	0.24	1.55
8	0.52	2.92	0.52	2.02	0.48	1.54
16	0.73	2.94	0.73	2.03	0.66	1.53
32	1.01	2.97	0.99	2.00	0.92	1.55
128	1.88	3.02	1.78	1.97	1.64	1.51
512	3.07	2.82	2.94	1.89	2.81 ·	1.52
1024	3.69	2.74	3.06	1.61	2.67	1.21
2048	4.39	2.71	5.26	2.21	4.58	1.57

Picric Acid.

Table LXXXVII.—*Molecular Conductivity.*

V.	0°.	15°.	25°.	35°.
32	193.0	260.2	303.7	345.1
128	201.1	272.4	319.9	365.2
512	207.6	280.9	329.6	377.5
1024	206.9	281.7	332.6	379.9
2048	203.5	277.1	325.6	372.7

Table LXXXVIII.—*Percentage Dissociation.*

V.	0°.	15°.	25°.	35°.
32	93.0	92.4	91.3	90.8
128	96.9	96.7	96.2	96.1
512	100.0	99.7	99.1	99.4
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Table LXXXIX.—*Temperature Coefficients.*

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	4.48	2.32	4.35	1.67	4.14	1.36
128	4.75	2.36	4.75	1.77	4.53	1.42
512	4.89	2.36	4.87	1.73	4.79	1.42
1024	4.99	2.41	4.89	1.74	4.93	1.48
2048	4.73	2.30	4.85	1.75	4.71	1.45

Propionic Acid.

Table XC.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
2	1.06	1.49	1.74	1.98
8	2.31	3.19	3.72	4.22
16	3.26	4.51	5.29	5.99
32	4.65	6.42	7.52	8.49
128	9.09	12.53	14.78	16.69
512	17.18	23.45	27.39	30.70
1024	23.49	32.09	37.58	42.29
2048	31.51	42.88	51.04	36.80

Table XCI.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
2	0.48	0.49	0.49	0.49
8	1.04	1.06	1.04	1.06
16	1.47	1.50	1.47	1.50
32	2.10	2.12	2.09	2.13
128	4.10	4.15	4.12	4.18
512	7.74	7.77	7.63	7.69
1024	10.6	10.6	10.5	10.6
2048	14.2	14.2	14.2	14.2

Table XCII.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.64	0.03	1.68	0.02	1.32
8	0.05	2.25	0.05	1.66	0.05	1.31
16	0.08	2.55	0.08	1.70	0.07	1.32
32	0.12	2.54	0.11	1.71	0.08	1.29
128	0.23	2.52	0.23	1.80	0.19	1.29
512	0.42	2.43	0.39	1.68	0.33	1.21
1024	0.57	2.43	0.55	1.71	0.47	1.25
2048	0.76	2.41	0.82	1.90	0.58	1.13

o-Nitrobenzoic Acid.
Table XCIII.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
32	98.15	120.5	132.2	140.6
128	146.9	184.9	205.6	222.6
512	187.5	244.1	278.3	307.8
1024	196.3	261.7	301.8	336.9
2048	200.8	267.4	312.2	351.8

Table XCIV.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
32	43.1	39.6	37.2	35.2
128	64.4	60.8	57.9	55.7
512	82.2	80.3	78.4	77.0
1024	86.1	86.1	85.0	84.2
2048	88.1	88.0	88.0	88.0

Table XCV.—Temperature Coefficients.

V.	0° to 15°.		15° to 25°.		25° to 35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	1.49	1.52	1.17	0.97	0.84	0.59
128	2.53	1.72	2.07	1.12	1.70	0.76
512	3.77	2.61	3.42	1.40	2.95	1.06
1024	4.36	2.22	4.01	1.53	3.51	1.16
2048	4.44	2.21	4.48	1.68	3.96	1.27

m-Nitrobenzoic Acid.

Table XCVI.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
128	40.10	56.85	67.66	77.56
512	71.95	101.0	120.0	137.1
1024	92.44	129.8	153.8	175.4
2048	115.1	160.7	190.5	216.7

Table XCVII.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
128	18.7	19.0	19.1	19.2
512	33.6	33.8	33.8	33.9
1024	43.1	43.4	43.3	43.4
2048	53.7	53.8	53.7	53.6

Table XCVIII.—Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
128	1.12	2.79	1.08	1.90	0.99	1.46
512	1.87	2.60	1.90	1.88	1.71	1.43
1024	2.49	2.69	2.40	1.85	2.16	1.40
2048	3.04	2.64	2.98	1.85	2.62	1.38

Discussion of Results.

We have already shown that widely different conclusions have been reached regarding the effect of temperature on the conductivity and ionization of electrolytes in aqueous solution.

For the purpose of arriving at something definite it was desirable to extend the work to as many different compounds as possible. The present investigation includes twenty-eight inorganic salts and six organic acids. The salts were so chosen as to have a wide range of physical and chemical properties, especially those of valence and the power of salts to crystallize with water of crystallization.

By glancing at any one of the preceding tables it will be seen that the molecular conductivity of electrolytes increases with rise in temperature from 0° to 35°; that conductivity increases with increase in dilution up to a certain maximum

value, and that dissociation increases with increase in dilution up to the point where the electrolyte is completely dissociated. These facts are, however, so well established by previous work that additional evidence seems almost unnecessary.

A maximum in the conductivity curve, as described by Sack,[1] Kohlrausch,[2] Noyes,[3] and others, was not observed at
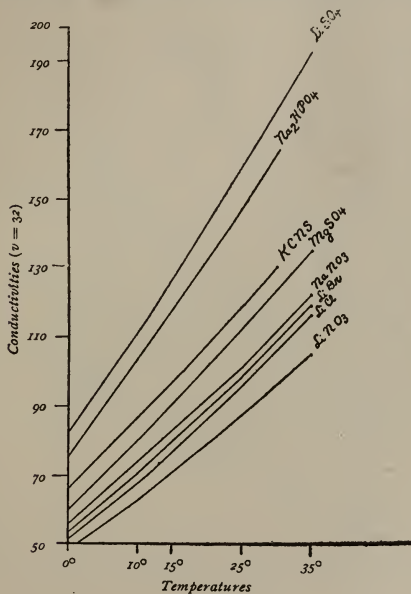
Fig. III.

any time during the progress of the work. This, however, was not to be expected, since a maximum conductivity generally occurs at much higher temperatures than those at which we worked.

With these preliminary observations we shall turn to the

[1] Wied. Ann., **43**, 212 (1891).
[2] Pogg. Ann., **154**, 215 (1875).
[3] J. Am. Chem. Soc., **26**, 134 (1904).

real questions at issue. In the first place: Is conductivity a linear function of the temperature? As is pointed out in the introduction, different conclusions have been reached by different experimenters. Our work goes to show that, except in the case of water, *conductivity is not a linear function of the temperature at any dilution with which we worked.* The increase in conductivity with rise in temperature is greater
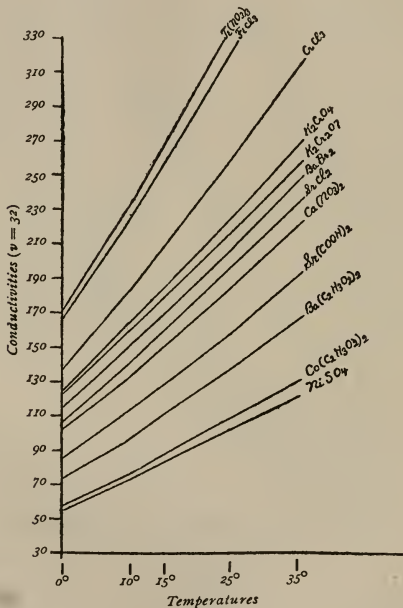
Fig. IV.

the higher the temperature. This becomes more apparent by observing the curves in Figs. III, IV, and V, where molecular conductivities are the ordinates and temperatures the abcissae. Water presents the only exception to this rule. In Fig. II the conductivity of water has been plotted against temperature, and as is seen the relation is a linear one from 0° to 35°.
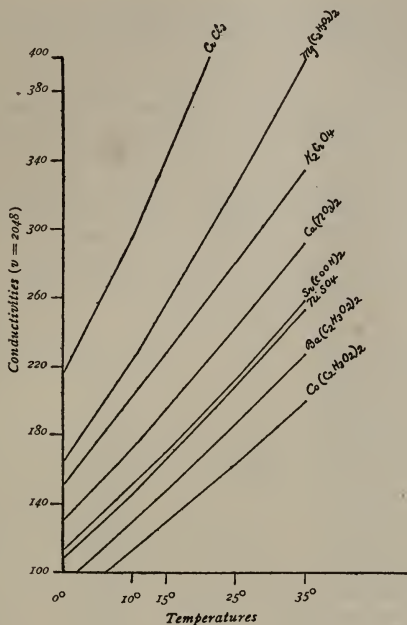
Fig. V.

The increase in the conductivity of electrolytes with rise in temperature is undoubtedly due, as has been pointed out by Jones,[1] largely to the fact that all electrolytes in aqueous solution are hydrated to a greater or less extent, and that rise in temperature diminishes the extent of this hydration. It is clear that when the ions become partly or wholly freed from the water attached to them, their mass, and probably their size, will be reduced. This will allow them to move through the solution with less friction and, consequently, increase the conductivity. Therefore, it is fair to conclude that the conductivity of those ions which are hydrated to the greatest

[1] THIS JOURNAL, **35**, 445 (1905).

extent in solution would be most affected by change in temperature. All of the experimental data, here given, support this conclusion.

In Table XCIX. is given a list of the substances investigated. They are arranged in the order of their increasing temperature coefficients. By referring to these tables it will be seen that those substances with little or no hydrating power are at the top, while those possessing a marked hydrating power appear towards the bottom of the list. Upon this hypothesis we may explain the fact that the change in conductivity with temperature is not a linear function in the case of ordinary electrolytes, while in the case of water it is a linear function.

Table XCIX.

Substance.	Temp. Coef., 0°–10°. $V = 2048$.	Temp. Coef., 25°–35°. $V = 2048$.
Lithium nitrate	1.76	2.07
Lithium chloride	1.92	2.31
Lithium bromide	1.94	2.34
Sodium nitrate	2.27	2.44
Potassium sulphocyanate	2.24	2.72
Nickel acetate	2.86	3.60
Cobalt acetate	3.03	3.56
Cobalt sulphate	3.75	4.51
Nickel sulphate	3.72	4.52
Barium acetate	3.33	4.04
Strontium formate	3.91	4.56
Disodium phosphate	3.68	4.44
Barium formate	3.76	4.76
Magnesium sulphate	3.74	4.58
Lithium sulphate	3.77	4.85
Potassium dichromate	4.13	4.81
Potassium chromate	4.93	5.44
Calcium nitrate	4.31	4.97
Strontium chloride	4.31	5.31
Cupric bromide	4.22	5.23
Barium bromide	4.45	5.24
Barium nitrate	4.02	4.90
Strontium nitrate	4.06	4.89
Lead nitrate	4.36	5.18
Chromium chloride	7.97	11.17
Chromium nitrate	8.49	11.29
Ferric nitrate	10.83	22.14
Ferric chloride	19.00	24.16

As has just been pointed out, the electrolytes whose ions are hydrated in solution will show a large increase in conductivity with rise in temperature. This is equivalent to saying that their conductivities are parabolic functions of the temperature. In the case of water it is difficult to see how the hydrogen or hydroxyl ions could become appreciably hydrated; and the fact that the conductivity of water increases regularly with rise in temperature goes to show that no such hydration exists, but that the increase in conductivity is conditioned chiefly by a change in the viscosity of the medium. This latter phenomenon we know to be a linear one with respect to temperature, and by *a priori* reasoning we would conclude that the conductivity of water, or of any entirely unhydrated electrolyte, if such existed, would also be a linear function of the temperature. Facts and theory are in perfect accord on this point.

Another factor, playing an important rôle in conductivity work, is hydrolysis. Scarcely too great emphasis can be laid on the fact that water is decomposed in the presence of a large number of substances in solution, and yet it is surprising to see how much conductivity work has been done where this fact has been overlooked or disregarded.

To ascertain the effect of hydrolysis on the conductivity of strongly hydrolyzed salts, we have included iron and chromium compounds in this work. By referring to the tables where the molecular conductivities of these compounds are given, it is seen that the increase in their conductivities at high dilutions is so abnormally large that one might think nothing but gross experimental error could account for it. It is also seen that their conductivities are disproportionately larger at higher temperatures. These results plainly show that hydrolysis is enormously increased with rise in temperature. Now the question arises: Is hydrolysis manifested only by salts of strong acids and weak bases, and *vice versa*, or where both acid and base are weak; or is it a phenomenon common to all electrolytes? The latter view is the one held by Ciamician,[1] Euler,[2] Bauer,[3] and others. In order to obtain

[1] Z. physik. Chem., **6**, 403 (1890).
[2] *Ibid.*, **21**, 257 (1896).
[3] *Ibid.*, **23**, 409 (1897).

evidence on this point let us again turn to the preceding tables. It is seen that in nearly every case the conductivity changes more or less suddenly from $V = 1024$ to $V = 2048$. The conductivity is by no means a constant at those dilutions, yet in the majority of cases the substances are thought to be completely dissociated. For these reasons we are convinced that nearly all, if not all, electrolytes are hydrolyzed in dilute solution.

Granting this fact, how would it affect the percentage dissociation as calculated by the formula: μ_v/μ_∞ ? It is clear that if hydrolysis takes place at high dilutions the value of μ_∞ as found is too large by that amount. For this reason α becomes smaller than it otherwise would. It is a well-known fact that hydrolysis is greatly accelerated by rise in temperature, and, consequently, the values for μ_∞ will grow proportionately larger as the temperature is raised. This will, of course, diminish the calculated value of the dissociation more and more the higher the temperature.

The above reasoning is based on the assumption that hydrolysis takes place to a greater extent in dilute than in more concentrated solutions. In case of weakly hydrolyzed compounds we should say that this is the case, for mass action then comes into play; whereas, with strongly hydrolyzed salts like the iron, lead, and aluminium compounds, the effect of hydrolysis would probably be more pronounced before high dilutions are reached. Referring to the tables of the iron salts we see that this theory is supported by the facts.

A summary of the results of the effect of rise in temperature on dissociation is given in Table C.

It is seen that the results are of the same general character as those obtained by Jones and West.[1] The fact that an increase in dissociation with rise in temperature is found with the iron salts, lead nitrate, and m-nitrobenzoic acid is doubtless due to hydrolysis, as is explained above.

For the reasons already mentioned it seems to us that the true effect of temperature on dissociation cannot be rigidly ascertained unless hydration, on the one hand, and hydrolysis,

[1] This Journal, **34**, 357 (1905).

Table C.

α decreases with rise in temperature.	α increases with rise in temperature.
Potassium sulphocyanate	Ferric chloride
Barium bromide	" nitrate
" formate	Lead nitrate
Sodium nitrate	*m*-Nitrobenzoic acid
Disodium phosphate	α independent of temperature.
Lithium nitrate	Potassium chromate
" chloride	Potassium dichromate
" bromide	Cupric bromide
" sulphate	Racemic acid
Calcium nitrate	Propionic acid
Strontium formate	α decreases in concentrated, but increases in dilute solutions.
Magnesium sulphate	
Nickel "	Barium acetate
Cobalt "	Cobalt "
Chromium chloride	Nickel "
" nitrate	α increases slightly in dilute solutions.
Trichloracetic acid	Strontium chloride
Picric acid	" nitrate
o-Nitrobenzoic acid	Barium "

on the other, are taken into account. It is a fact, however, that many electrolytes are affected only to a relatively small extent by these influences, and that the value for dissociation calculated without taking these into account is not far from the correct value.

When we examine the temperature coefficients expressed in conductivity units, we find that, without exception, they increase as dilution increases, and for every salt they increase with rise in temperature; but the organic acids, on the other hand, have decreasing temperature coefficients with rise in temperature. This is more clearly seen by reference to Fig. 6, where coefficients are the ordinates and temperatures the abscissae.

The temperature coefficients expressed in percentages, on the other hand, invariably decrease with rise in temperature. The fact that temperature coefficients of all salts increase with rise in temperature, whereas both organic and inorganic acids have decreasing temperature coefficients, is easily explained

by the hydrate theory of Jones. The metallic cations are probably the ones that are chiefly hydrated in solution, and when the temperature is raised this hydration is diminished, thus greatly increasing the ionic mobility, while no such increase is possible where metallic ions are absent.
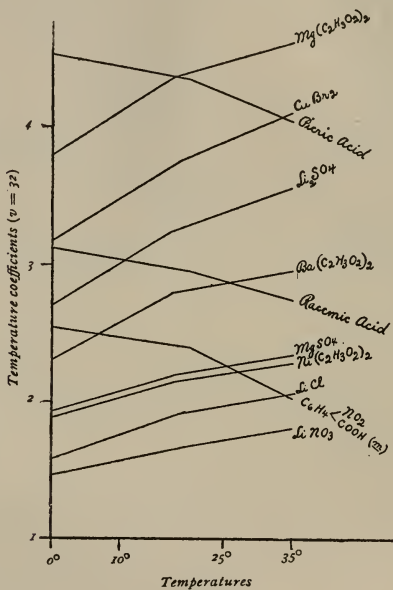
Fig. VI.

During the progress of this work we noticed a striking phenomenon in the telephone that should be mentioned. A short time after the circuit was closed, thus allowing the current to pass through the cell containing the electrolyte, a sudden increase in the loudness of the tone was noticed when the key was held near the node on the bridge. This phenomenon was at first thought to be due to polarization, but later,

when the same effect could be obtained with any solution, even with redistilled water, and since no noticeable change in conductivity could be detected as a result of it, we concluded that this phenomenon is novel in character, and as far as we know has not been described before. The time for this loudness to come on varied from a few seconds to eight or ten minutes, depending upon the nature of the electrolyte.

It is futile to speculate what might be its cause until more experimental evidence is obtained. One suggestion that might have an element of truth in it is the following: The kinetic vibrations of the ions may be influenced by the electrical stress, set up within the solution, in such a way that they will be brought to take place in the direction of the lines of force present. This idea could be illustrated by the molecular arrangement thought to exist in a permanent magnet.

Conclusions.

The following points have been verified or established by the present work:

1. The molecular conductivity of electrolytes in aqueous solution increases as a parabolic function of the temperature from 0° to 35°.

2. Conductivity increases with increase in dilution.

3. With increase in dilution dissociation increases up to a maximum value where it is complete.

4. Hydrolysis is a formidable source of error in obtaining the true value for μ_∞ and, consequently, in obtaining the true dissociation.

5. Disregarding the effect of hydrolysis, dissociation decreases with rise in temperature.

6. The conductivity of water is a linear function of the temperature.

7. Salts that are strongly hydrated in solution show a greater increase in conductivity with rise in temperature than the salts that are slightly hydrated.

8. The temperature coefficients, expressed in conductivity units, increase with rise in temperature. Those of the organic acids are exceptions.

9. The temperature coefficients expressed in percentages decrease with rise in temperature.

10. The temperature coefficients of compounds with similar properties vary in a similar manner with change in temperature.

We are extending, in this laboratory, this investigation to all of the more common electrolytes, organic and inorganic. We are studying the temperature coefficients of conductivity and of dissociation over the range of temperatures extending from 35° to as near the boiling points of the solutions as it is possible to go.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1908.

REVIEWS.

A TREATISE ON CHEMISTRY. By H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol II.—THE METALS. London: Macmillan and Co. 1907. pp. 1436. Price, $7.50.

The treatise of Roscoe and Schorlemmer has always been regarded as the most reliable, and, all things considered, the most satisfactory treatise on chemistry. The last edition, Vol. II., appeared in 1897. In regard to this, the fourth edition, Sir Henry Roscoe says: "Much new and important matter with regard to the Metals and their Compounds has come to light in the ten years since the last edition of this work appeared, and in the present volume care has been taken to include all the more important points connected with the recent discoveries."

The earlier editions are so well and so favorably known that general comment is uncalled for. A fairly complete examination of this new edition shows that it embodies the important later discoveries, including those in the field of physical chemistry. Whether the book is sufficiently saturated with the modern physical conceptions is a question that can be answered only by physical chemists. Extremists will perhaps feel that the authors have not gone far enough into the ionic field.

The attitude of the authors towards the later developments appears to be appreciative and fair. Take, for example, this passage referring to the corpuscular theory of the constitution of the atom: "This theory is admirably adapted to explain the phenomena of electrolysis and all reactions which occur between ions, as well as all cases of combination between electro-positive

and electro-negative elements. Considerable difficulties, however, arise when it is applied to elements which are not markedly electro-positive or electro-negative, and especially to those compounds in which a number of the atoms of the same element are combined together. In such a simple compound as ethane, CH_3–CH_3, for instance, it is necessary to suppose that one of the carbon atoms acts as the positive and the other as the negative element, although no difference between the two has been recognized chemically. Similar considerations hold with regard to the molecules of the elements themselves, many of which are composed of two atoms of the element united together.

"These difficulties have not yet been entirely surmounted, although attempts have been made to devise a consistent empirical system which will be in accordance with these electrochemical requirements, by supposing that each element possesses a definite and limited power of combining both with relatively positive and with negative elements."

The chapter dealing with the "Metals of the Rare Earths" will be especially welcome, as it no doubt is the best summary of the work on this subject. In regard to the group dysprosium, holmium, erbium, and thulium, the authors say: "The terbia originally isolated from crude yttria by Mosander subsequently received the name of *erbia* (Berlin), and has been shown by Soret, Cleve, Thalén, and Lecoq de Boisbaudran to consist of at least four earths, the true *erbia*, *holmia*, *thulia*, and *dysprosia*. The salts of all these show absorption bands, but it is doubtful if any one of the four, with the possible exception of dysprosium, is an individual substance. Erbium forms a rose-colored oxide and salts of the same color, which in solution show absorption bands, while the salts of dysprosium are green or yellow."

In regard to ytterbium they say: "Doubts as to the individuality of the ytterbium compounds have been expressed by Auer von Welsbach."

The subject of "The Radioactive Elements" is dealt with in twenty-eight pages in a very clear way. The recent very remarkable results obtained by Cameron and Ramsay on the formation of lithium salts from copper salts by the action of radium emanation are included. The chapter concludes with these words: "The atom must now be regarded as an aggregate of simpler forms of matter, possessing enormous potential energy. This aggregate may, under conditions which we are not yet able to control, break down into simpler forms, a large amount of energy being evolved in the change. Hence the unalterability of the atom postulated by Dalton must be modified, and the atom must be regarded as a complex, but of a

higher order than the chemical compounds formed by the union of atoms with each other.'' It is impossible at present to establish a more precise characterization of this higher order of complex substances than is expressed in the statement that the decomposition of an atom is beyond our control and that the energy changes are of a higher order of magnitude than is the case with ordinary compounds.

"These discoveries, however, while opening out new views as to the constitution of matter, are in no degree inconsistent with the well-established facts of chemical combination or with the application of them to Dalton's atomic theory."

Taking this book all in all, it can be spoken of only in the highest terms. It ought to be in every chemical library, whether that library is large or small.   I. R.

SPECTRUM ANALYSIS. By JOHN LANDAUER. Second Edition. Re-written by J. BISHOP TINGLE, PH.D., F.C.S. New York: John Wiley & Sons. 1907.

This book is an enlarged and rewritten translation of the German original which first appeared in 1898. Its purpose may, perhaps, best be stated by quoting the words of the translator in his "Preface to the Second Edition." He says, "In judging it (*i. e.*, this book) regard should be had to its object. It does not pretend to be an exhaustive work on the subject, but merely an elementary guide to those who, with relatively little knowledge of physics, desire to understand something of the general scope and methods of spectrum analysis and to make practical use of the spectroscope;......" The book begins with an historical review of the science of spectroscopy and a bibliography of works on spectrum analysis. This is followed by chapters dealing with the following subjects: Physical Properties of Light, Spectroscopes, Spectroscopic Instruments for Special Purposes, Spectroscopic Adjuncts, Spectra, Spectra of the Elements, Absorption Spectra, Solar Spectrum, Other Celestial Bodies.

Altogether, the book serves very well as an introduction to spectrum analysis. The main fault which might be found with it is that, in some respects, it is not sufficiently modern. This criticism applies mainly to the absence of a treatment of the spectroscopic analysis of complexes—a subject which, in the estimate of the reviewer, ought to form a most important part of the book. The two fundamental arguments which are at the basis of the entire science of spectrum analysis are, (1) that each element produces a spectrum which is absolutely characteristic, (2) that the spectroscope is capable of detecting the existence of elements which are present in quantities much

too minute for chemical analysis. The first essential to a practical application of spectrum analysis is an intimate knowledge of the characteristic appearance of the spectra of the elements—and it must be admitted that, in the present volume, this part of the subject is well treated. Not only is the descriptive part well done, but the wave lengths of the principal lines, determined by numerous observers who have based their determinations upon various standards, have all been recalculated so as to be in accord with Rowland's values. In addition, the complete list of Rowland's determinations of the wave lengths of the Fraunhofer lines (extending from λ 3000 to 7714 A. V.) is given.

The principal shortcomings of the book are to be found in the treatment of the subject-matter coming under the second argument previously referred to. The problem which most often confronts the spectroscopist is the analysis of a complex such as a bit of rock or meteorite, or a mixture of unknown gases. Now it is a well-known fact that, in the spectrum of a complex of elements, certain elements obliterate more or less completely the spectrum of the others, even though the latter be present in relatively large quantities. In recent years considerable attention has been paid to this matter. Methods have been developed for bringing out the easily marked spectra, and the wave lengths of those lines which are most liable to persist have been determined—thus making possible the detection of those elements which would otherwise remain undiscovered. The fact that the great majority of books on spectrum analysis devote but little space to this most important branch of the subject would make its discussion in a modern treatise highly desirable.

A careful perusal of the book has yielded but few misprints or misstatements, and as those which have been found do not materially influence the usefulness of the text, there is not much need of pointing out these slight defects individually. Considering the book as a whole, it well fulfils the purpose for which it was written and ought to be of great service to chemists.

A. H. PFUND.

A LABORATORY OUTLINE FOR DETERMINATIONS IN QUANTITATIVE CHEMICAL ANALYSIS. By ALBERT F. GILMAN, S.B., A.M., Professor of Chemistry, Ripon College, Ripon, Wisconsin, Easton, Pa.: Chemical Publishing Co. 1908. pp. 88.

This little book is intended to be used as a combined laboratory guide and record book of experiments performed by students just beginning work in quantitative analysis. The more common methods of determining the metals and some of the

acids are given.   The rather meagre directions are supplemented at the end of each determination by references to Fresenius and Classen and by questions concerning details of the method of procedure.   The directions are in general clear, although the English could in many cases be improved.   C. A. R.

UEBER DIE SCHICHTUNGEN BEI DIFFUSION.   Eine Voruntersuchung, von Raphael Ed. Liesegang.   Düsseldorf. 1907.   pp. 66.

This little pamphlet records a number of interesting and probably important observations, in reference to the layers that are formed in various processes of diffusion, especially into gelatine.   A number of beautiful plates are given, showing the various layers that were observed.   H. C. J.

AMERICAN

CHEMICAL JOURNAL

[Contributions from the Chemical Laboratory of Lehigh University.]

VII.—ABNORMAL BIOCHEMICAL PRODUCTS OF THE RUE ANEMONE.

By Frederick S. Beattie.

During certain investigations into the flora of northeastern Rhode Island, a new phase of the subject of plant life and its chemical products came into prominence. Vegetable growths form a fairly important source of numerous chemical compounds, of which some few have from time to time been obtained synthetically, but of which the greater part still offers subjects for exhaustive investigation. The case in question differs from that of such compounds, in that it relates to bodies which so far have been regarded as purely synthetic, but which now appear in the light of substances also occurring naturally.

The plant known variously as *Syndesmon thalictroides Hoffmg.*, *Anemonella thalictroides Spach*, and *Thalictrum anemonoides Michx.*, which is commonly known as rue anemone, in its normal condition, as far as the author has been able to examine it, contains no cyclic compounds, either with or without nuclear nitrogen; the nitrogenous content is exceedingly small, too small, in fact, for satisfactory estimation;

and the major content of the dry plant, beside vascular tissue, is apparently starch, chlorophyll, and some vegetable albuminous matter. The material under consideration consisted of the above-mentioned species; not in normal condition, but showing marked fasciation.[1] The species in this condition was found, in point of life products, to depart in noteworthy degree from the normal, containing a high percentage of quinoline derivatives. Fuller mention of the details of this departure will be made after the investigation of the products in question has been described.

Experimental.

Extraction and Separation of the Biochemical Products.—Two hundred and thirty grams of the finely cut plants, dried at 120°, were extracted repeatedly with boiling dried ether, and the ethereal extract subjected to distillation from the water bath. A gray, crystalline residue was obtained, weighing 38.7 grams. This was dissolved in 200 cc. boiling absolute ether, filtered hot to remove a small quantity of a blackish impurity, and cooled. Small, colorless crystals were deposited sparingly. After one-half hour, as their quantity did not increase perceptibly, the mixture was filtered, the crystals washed with a little cold absolute ether, and dried. They were thus obtained as small white leaves, weighing 5.3 grams and melting at about 250°. The ethereal filtrate was evaporated to crystallization, whereby a mass of fine white needles was obtained, weighing 32.4 grams and melting at 88°. The substances, therefore, were clearly different. As the high melting body was found to be somewhat soluble in hot acetone, the ground plants, already extracted with ether, were now exhausted with boiling acetone, and this extract distilled from the water bath as before. A further amount of the high melting substance, weight 8.1 grams, was thus obtained in small white leaves melting at 251°. Further extraction of the residue with benzene, chloroform, ethyl and methyl alcohol, and ligroin, gave nothing. The two lots of the sub-

[1] A pathological condition in which the malformed plant displays a flattening or lateral compression of parts which are in cross section usually circular; *e. g.*, the stem, tubers, ovaries.

stance melting at about 250° were treated separately with
dilute sodium carbonate solution and with dilute ammonia
water, in which they dissolved easily. A neutral solution of
the substance in ammonia water gave a white precipitate
with silver nitrate. As the substance appeared to be an acid,
it will be referred to hereafter as the high melting acid, and
taken up later in this paper. The body which melted at
about 88° did not dissolve in dilute sodium carbonate or
ammonia water, neither did it dissolve rapidly in a 10 per cent
solution of caustic soda. It will therefore be designated tem-
porarily as the neutral substance.

Purification and Properties of the Neutral Substance.—The
major part of the extracted compounds, which was obtained
by evaporation of the ethereal filtrate, melted at 88°–89°.
It was recrystallized several times from a mixture of three
volumes acetone and one volume water, this mixture being
found to give better results than either ether or pure acetone.
After one recrystallization the melting point rose to 93°.0;
after the second, it was 93°.4, at which it remained after
three more recrystallizations. From the original 32.4 grams
were thus obtained 29.7 grams of the purified product.
Evaporation *in vacuo* below 80° of filtrates from these re-
crystallizations gave a thick yellow oil weighing 2.6 grams,
nonvolatile with steam, not solidifying in a freezing mixture,
and resinifying after standing two weeks in a stoppered bottle.

The neutral substance, thus purified, dissolved very easily
in absolute and 96 per cent alcohol, easily in acetone, ether,
benzene, moderately in glacial acetic acid, but not at all in
hot or cold water. It possessed a peculiar, very fragrant and
persistent odor, somewhat like that of the yellow melilot.
From dilute acetone it crystallized in shining white needles,
3–4 mm. long. Qualitative analysis showed that the substance
contained nitrogen, but no sulphur. Burned on platinum
foil, it left no ash.

I. 0.2314 gram gave 13.4 cc. N at 18°.0 C. and 756.2 mm.[1]

[1] In this, as in all the other nitrogen determinations, the gas was measured over
a 50 per cent solution of potassium hydroxide.

II. 0.3026 gram gave 0.7314 gram CO_2 and 0.1326 gram H_2O.

Molecular weight determinations by the freezing point method gave the following results:

	Acetic acid. Grams.	Substance. Gram.	Δ.	Mol. wt.
I.	10.0000	0.1687	0°.309	212
II.	10.0000	0.1423	0°.264	210
III.	10.0000	0.1946	0°.352	216
			Mean,	213

It was impossible to calculate from these data a satisfactory formula for the substance, the formulae agreeing best with the results being $C_{11}H_9NO_3$, with a molecular weight of 203, and $C_{11}H_{10}NO_3$, with a molecular weight of 204. It was therefore thought advisable to obtain a better idea of the structure of the neutral substance, in the hope that some light might thereby be thrown upon the above difficulty.

Hydrolysis of the Neutral Substance.—The substance, dissolved in benzene, did not add bromine. On standing in the cold with dilute (5 per cent) aqueous potassium hydroxide it dissolved very slowly, without evolution of gas. The solution thereby obtained was clear, colorless, odorless; on acidification with hydrochloric acid it gave a copious white precipitate, which, with much excess of acid, redissolved slowly. This acid solution was made alkaline with 10 per cent caustic potash, and dilute hydrochloric acid added cautiously till precipitation was complete. The filtered and washed precipitate dissolved very readily in dilute caustic alkalies, and in alkaline carbonates with evolution of carbon dioxide. Ten grams of the neutral substance were therefore hydrolyzed by warming at 90° with a solution of 10 grams caustic potash in 200 cc. water, the mixture being heated on the water bath under a return condenser, with almost continuous shaking. The substance melted in contact with water below 80°, although its proper melting point was over 90°. After being heated and shaken twenty minutes, the oily layer had disappeared entirely, and the solution was

clear. As it was suspected that the neutral substance might be an ester, the condenser was now reversed, and the mixture heated to gentle boiling over a small flame until 30 cc. had distilled over. This distillate will be taken up later. The liquid remaining in the flask was now cooled, and treated carefully with dilute hydrochloric acid. A white precipitate was obtained as before, which, after standing one-half hour, was filtered, washed, and dried. Its weight (crude) was 9.21 grams: recrystallized three times from acetone, it was obtained in the form of silky, white needles, weighing 8.79 grams. From its behavior toward alkalies it was clearly an acid. It melted sharply at 319°.4, after three recrystallizations and after repeated solution in soda solution and subsequent precipitation therefrom by hydrochloric acid. On melting, it became brown, and gave off bubbles of gas. Heated slowly, it sublimed below its melting point. It dissolved sparingly in hot alcohol, ether, benzene, and chloroform, rather easily in hot acetone and glacial acetic acid, not at all in hot water.

I. 0.3293 gram gave 20.4 cc. N at 17°.1 and 759.6 mm.

II. 0.1823 gram gave 0.4244 gram CO_2 and 0.0608 gram H_2O.

III. 0.1989 gram gave 0.4627 gram CO_2 and 0.0666 gram H_2O.

Molecular weight determinations by the freezing point method gave the following results:

	Acetic acid. Grams.	Substance. Gram.	Δ.	Mol. wt.
I.	10.0000	0.1821	0°.388	183
II.	10.0000	0.1249	0°.255	191
			Mean,	187

The values obtained approximate very closely to the formula $C_{10}H_7NO_3$, which has a molecular weight of 189.

	Calculated for $C_{10}H_7NO_3$.	Found. I.	II.
C	63.49	63.49	63.44
H	3.70	3.71	3.72
N	7.41	7.34	....

About 0.5 gram was converted into the barium salt by treatment with water and careful addition of barium hydroxide solution, phenolphthalein being used as the indicator. The solution was then concentrated to a small bulk and the colorless crystals which separated abundantly were filtered, recrystallized once from hot water, in which the salt was sparingly soluble, and dried at 110° to constant weight.

0.4826 gram salt gave 0.2186 gram $BaSO_4$.

	Calculated for $C_{20}H_{12}N_2O_6Ba$.	Found.
Ba	12.91	12.86

The lead salt was prepared by mixing a neutral solution of the acid in ammonia water with lead acetate solution. It was obtained as a white, amorphous powder, insoluble in water. It was not analyzed.

Thermolysis of the Acid $C_{10}H_7NO_3$ to the Base C_9H_7NO.—As it had already been noticed that the acid, when fusing, gave off a gas, attention was next turned to this point. By careful fusion of a small quantity of the acid, the gas formed was proved, by testing with baryta water, to be carbon dioxide. Three and four-hundredths grams were then heated carefully in a tared flask, in a current of hydrogen, to 320°, and then to 325°, where the temperature was maintained for half an hour, tests being made from time to time for the presence of carbon dioxide in the escaping hydrogen. Nearly all the carbon dioxide was expelled in the first ten minutes, entirely so in twenty minutes. The reaction product was then allowed to cool, still in an atmosphere of hydrogen. The product solidified on cooling to a pale brown, crystalline mass, weighing 2.12 grams. Recrystallized from benzene it was obtained in white, glistening needles, which after three recrystallizations melted constantly and sharply at 208°.5. As a qualitative examination showed the presence of nitrogen, the substance was analyzed, with the following results:

I. 0.2817 gram gave 23.1 cc. N at 20°.0 C. and 760.4 mm.

II. 0.1879 gram gave 0.5129 gram CO_2 and 0.0824 gram H_2O.

III. 0.2006 gram gave 0.5478 gram CO_2 and 0.0901 gram H_2O.

The compound was clearly a base, as it dissolved easily in the halogen acids, also in sulphuric and nitric acids, all dilute. It was not possible to obtain salts in this manner. The hydrochloride was obtained as a white crystalline powder by passing dry hydrochloric acid gas into a saturated solution of the base in benzene. The crystals, dried *in vacuo* over caustic soda, gave, on analysis, the following result:

0.2166 gram gave 0.1697 gram AgCl = 0.0432 gram HCl.

On the assumption that the substance in question is a monacid base, the molecular weight of the hydrochloride would be 183, and that of the base alone would be 146.

On addition of platinic chloride solution to a rather strong solution of the base in hydrochloric acid, the chloroplatinate was precipitated as a yellow crystalline powder. This was filtered off, washed with cold water, in which it was only sparingly soluble, and dried *in vacuo* over sulphuric acid. Analyzed for platinum, it gave the following:

0.6128 gram gave 0.1706 gram Pt.

The molecular weight of the chloroplatinate is therefore 700, of the base, 145, which agrees well with the provisional 146 given above. From the data now in hand, the formula of the base is C_9H_7NO.

	Calculated for C_9H_7NO.	Found. I.	II.
C	74.48	74.44	74.47
H	4.83	4.87	4.99
N	9.65	9.63	....

Reduction of the Base C_9H_7NO to Isoquinoline.—It was seen at once that this formula was that of an oxyquinoline; furthermore, the melting point, 208°, agreed exactly with that assigned to 1-oxyisoquinoline. About 3 grams, prepared as before by fusing the acid $C_{10}H_7NO_3$ in an atmosphere of hydrogen, were distilled with excess of zinc dust and pumice from a hard glass tube, in a current of hydrogen. A yield of about 40 per cent was obtained of a pale yellow oil, which, when

frozen and pressed out upon cold porous porcelain, appeared in a colorless, crystalline condition, melting sharply at 24°.5, and boiling, as far as could be determined from the small quantity at the author's disposal, at about 235°–237°. The melting and boiling points of isoquinoline are given as 24°.6 and 240°.5, respectively. In order to confirm the identity of the substance, a solution of the hydrochloride of the base (clearly a base, as it dissolved readily in dilute mineral acids, and not at all in even concentrated caustic alkalies) was precipitated with strong platinic chloride solution. The chloroplatinate thus formed, when recrystallized from hot water, was obtained as a mass of fine yellow needles of a decided reddish tinge, melting sharply at 263° with decomposition.

0.5612 gram of salt dried *in vacuo* gave 0.1552 gram Pt.

	Calculated for $(C_9H_7N.HCl)_2PtCl_4.2H_2O$.	Found.
Pt	27.67	27.65

0.4091 gram of salt dried at 170° gave 0.1186 gram Pt.

	Calculated for $(C_9H_7N.HCl)_2PtCl_4$.	Found.
Pt	27.19	28.99

The molecular weight of the base is therefore about 131. That of isoquinoline is 129.

The picrate of the base formed yellow needles, rather difficultly soluble in cold absolute alcohol. It melted at 221°–222°. Isoquinoline picrate melts at 222°–223°.

The sulphate was prepared by adding sulphuric acid (1 mol.) dissolved in ether, to a solution of the base (1 mol.) in absolute alcohol, and evaporating to crystallization. So prepared, it formed small, white, shining leaves, moderately soluble in hot, more difficultly in cold, alcohol. The vacuum dried salt, on analysis, gave the following result:

0.4447 gram gave 0.4549 gram $BaSO_4$.

	Calculated for $C_9H_7N.H_2SO_4$.	Found.
S	14.09	13.76

Constitution of the Acid $C_{10}H_7NO_3$.—From the experimental data now at hand, the relationship of the acid $C_{10}H_7NO_3$,

derived by hydrolysis from the neutral body, to the base isoquinoline becomes clearer. As on fusion it passes over, with loss of carbon dioxide, to oxyisoquinoline, or isocarbostyril, it is clearly a carbonic acid of oxyisoquinoline, and, as the analyses show, a monobasic acid. There is no hesitation in designating it as 1-oxyisoquinoline-3-carboxylic acid or isocarbostyril-3-carboxylic acid, as the melting point, 320°, agrees exactly with that given in the literature.

Study of the Aqueous Distillate from Hydrolysis.—The 30 cc. of distillate obtained fom the potassium hydroxide hydrolysis of the neutral body were united with a second 30 cc. obtained similarly from hydrolysis of another 10 gram lot of the neutral body, and the mixture was fractionated repeatedly with great care. After nine fractionations through a small Hempel column, the products resolved themselves into three parts; a fraction boiling constantly at 66°–67°, weighing 0.8 gram, one boiling at 75°–80°, weighing 0.7 gram, and the residue, boiling constantly at 100°, weighing about 56 grams. The two lower boiling fractions possessed characteristic alcoholic odors. Both responded to the iodoform test, the 66°–67° fraction yielding traces only, the 75°–80° fraction giving iodoform abundantly. They were identified as methyl alcohol and ethyl alcohol, respectively, by conversion into esters of paranitrocinnamic acid, of known melting point. It was intended to prepare their esters with s-trinitrobenzoic acid, but the s-trinitrobenzoyl chloride destined for that purpose was lost by an accident, and as no more trinitrobenzoic acid was at hand, recourse was had to paranitrocinnamyl chloride. The lower boiling fraction, 0.32 gram (1′ mol. calculated for CH_3OH), was treated with 2.12 grams (1 mol.) of phosphorus pentachloride, with cooling; the reaction product was then heated at 100° for ten minutes to complete the reaction, cooled, and treated with ice water. A white, crystalline solid was precipitated, which was filtered off, washed well, and dried. It melted at 159° C. Recrystallized twice from pure acetic ester, it melted constantly at 161°.3. The melting point of paranitrocinnamic methyl ester is 161° C. Forty-six hundredths gram of the higher boiling

fraction (1 mol. calculated for C_2H_5OH), was treated similarly with 2.12 grams (1 mol.) of phosphorus pentachloride. The product in this case was a crystalline, slightly yellowish powder, which melted at 135°–136°. Three recrystallizations afforded a pale yellow ester which melted constantly at 138°.4 C., the melting point of paranitrocinnamic ethyl ester being 138°.5.

Identity of the Neutral Substance.—The neutral body, in view of the results already obtained, is evidently a mixture of esters of 1-oxyisoquinolinecarboxylic acid since on heating with aqueous potassium hydroxide it splits up into the acid just mentioned and at least two well identified alcohols, methyl and ethyl. Analysis of the neutral substance, which may now be called the ester mixture, gave values which it was difficult to reconcile with any particular formula. The methyl and the ethyl ester of the oxyisoquinoline acid would give the following values (the analysis of the ester mixture being subjoined):

	Calculated for methyl ester.	Calculated for ethyl ester.	Found for ester mixture.
C	65.04	66.36	65.92
H	4.43	5.07	4.87
N	6.89	6.45	6.81

By inspection, it will be seen that the figures actually obtained are what might be expected from a mixture of the two esters. It was not found possible, with the limited amount of mixture remaining, to effect a separation of the esters by crystallization, nor even so to alter their relative proportions as to change the melting point of the mixture. Such cases are hardly infrequent, *e. g.*, the nitrobenzaldehydes, ortho and meta. That the two esters were at least present in, if not entirely constituting, the ester mixture has already been made clear.

Study of the High Melting Acid.—The two portions of the high melting acid, weighing together 13.4 grams, were recrystallized from acetone-ether. After one recrystallization they melted at 253°; after the second, at 254°.3; subsequent recrystallizations failed to alter the melting point.

The acid dissolved somewhat in both hot ether and hot acetone; in cold ether it was insoluble, in cold acetone difficultly soluble; easily soluble in hot, less so in cold, alcohol. Qualitative examination showed nitrogen to be present, sulphur to be absent. Burned on platinum it gave no residue. Analysis gave the following:

I. 0.1604 gram gave 10.21 cc. N at 19°.2 C. and 761.4 mm.

II. 0.1733 gram gave 0.4485 gram CO_2 and 0.0851 gram H_2O.

Determinations of the molecular weight gave the following values:

	Phenol. Gram.	Substance. Gram.	Δ.	Mol. wt.
I.	12.0071	0.1620	0°.541	187
II.	12.0071	0.1413	0°.474	186
			Mean,	186.5

According to these data the formula of the acid would be $C_{11}H_9NO_2$, the molecular weight of which, 187, is almost exactly that found.

	Calculated for $C_{11}H_9NO_2$.	Found.
C	70.59	70.05
H	4.81	4.81
N	7.48	7.50

The silver salt was prepared by mixing a neutral solution of the acid in ammonia water with silver nitrate solution, and was obtained as a white, granular precipitate. After being well washed and dried *in vacuo*, it was analyzed for silver with the following results:

0.2181 gram gave 0.0799 gram Ag.

	Calculated for $C_{11}H_8NO_2Ag$.	Found.
Ag	36.73	36.66

Base from the Acid $C_{11}H_9NO_2$.—The persistent presence of nitrogen in this, as well as in the other compounds studied, led the author to believe that this body also was a heterocyclic compound referable finally to quinoline. The preparation of the parent hydrocarbon confirmed this belief.

Approximately equal weights of the barium salt of the acid and of barium hydroxide, both thoroughly dried, were distilled rapidly from a hard glass tube through which was passed a current of hydrogen. About 65 per cent of an oil came over, which possessed a pale yellow color and characteristic quinoline odor. On being strongly cooled, it solidified; after being pressed out in that condition upon cold porous porcelain, it was found to melt at $9°-12°$, and to boil above $240°$. It dissolved readily in dilute mineral acids, not at all in even concentrated caustic alkalies, and was therefore of basic nature. It contained nitrogen. The analysis follows:

I. 0.2007 gram gave 16.72 cc. N at $20°.0$ C. and 760.6 mm.

II. 0.1623 gram gave 0.4991 gram CO_2 and 0.0922 gram H_2O.

III. 0.0989 gram gave 0.3039 gram CO_2 and 0.0564 gram H_2O.

	Calculated for $C_{10}H_9N$.	I.	II.
		Found.	
C	83.91	83.87	83.82
H	6.29	6.31	6.33
N	9.79	9.78	....

The chloroplatinate was prepared in the usual manner. As it evidently contained water of crystallization, it was dried to constant weight at $140°$. On analysis,

0.4067 gram gave 0.1178 gram Pt.

This gives the molecular weight of the base as 132, which agrees moderately well with 143, the value derived from the combustions. The formula of the base is therefore $C_{10}H_9N$, which is that of a methylquinoline or methylisoquinoline. The picrate and the iodomethylate of the base were prepared, with the hope of obtaining some evidence as to the nature of the base. The picrate melted sharply at $187°$. The iodomethylate, prepared by heating equal weights of base and methyl iodide in a sealed tube at $80°$ for two hours, was obtained as a yellow crystalline deposit, which, pressed out upon porcelain and recrystallized from absolute alcohol, melted constantly at $221°$. The melting point of these two

characteristic derivatives indicate that the base is *py*-3-methylquinoline, and that the high melting acid must be a carboxyl derivative of that hydrocarbon. The melting point, 254°, agrees with that given by Miller[1] for *py*-3-methyl-quinoline-4-carboxylic acid. Its identity as such is confirmed by the fact that the only other known methylquinoline-carboxylic acid, which is derived from *py*-2-methylquinoline, namely the 3,2-acid, melts at 144°, and decomposes at 160° into carbon dioxide and its parent base, which the acid in question did not do of itself even at 260°. Miller states that the 3-methylquinolinecarboxylic acid is insoluble in ether. The author has found it to be rather sparingly soluble in boiling ether, but insoluble in even warm ether. In all other points his acid agrees with Miller's.

Conclusion.

The summary may be briefly stated thus: In fasciated plants of the species *Syndesmon thalictroides Hoffmg.* were found 1-oxyisoquinoline-3-carboxylic acid, in the form of its methyl and ethyl esters, and *py*-3-methylquinoline-4-carboxylic acid in the free state. The occurrence of these compounds here is of peculiar interest for three reasons:

(1) The two acids have been regarded, to the present, as purely synthetic products, and now appear for the first time as biochemical products.

(2) The biosynthesis of these two acids, as well as of other compounds of like nature, by this species, either normal or abnormal, has been heretofore unobserved.

(3) The percentage of the products investigated is astonishingly high: about 20 per cent of the dry plant.

No mention exists in the literature, as far as I can find, of investigations in the *Ranunculaceae* of this section.

All plants from which the material studied was derived were fasciated to an extreme degree, and constituted a sharply defined colony. Experiments performed with normal plants from the same wooded slope, within fifty feet of the fasciated colony, and living under exactly the same conditions of

[1] Ber. d. chem. Ges., **23**, 2257.

moisture, shade, drainage, etc., afforded no trace of the compounds obtained from the diseased plants. The soil throughout the whole tract under inspection was of uniform quality, the percentage of nitrogen in specimens of soil taken at random from seventeen spots within the said tract, and dried at 110°, ranging from 0.86 to 0.92 per cent.

It would be tempting to speculate upon possible explanations; but sufficient experimental data are not at hand to justify one in doing so. Experiments made later by the author seem to indicate that the substances which form the subject of this investigation were coincident, but not necessarily concomitant, with pronounced fasciation of the species. Results already obtained with diseased specimens of another species make it clear that abnormal chemical products often do accompany grave physical malformations; but more than this one cannot at present venture to say.

Work of similar nature, involving other species of the northeastern United States, is being carried on by the author.

SOUTH BETHLEHEM, PENNA.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND CINNAMYLIDENE ESTERS. II. REACTIONS WITH METHYL α-PHENYLCIN-NAMYLIDENEACETATE.

BY MARIE REIMER AND GRACE POTTER REYNOLDS.

In a previous paper[1] it was shown that the reaction between Grignard's reagent and methyl cinnamylidenemalonate consists entirely in 1,4 addition. It was pointed out that the course of the reaction was undoubtedly influenced by the carboxyl group in the α position, as negative groups in this position are known to increase the tendency toward 1,4 addition. In continuing the study of cinnamylidene esters, with a view to

[1] THIS JOURNAL, **38**, 227.

determining the influence of the second ethylene linkage on the reactivity of the conjugated system, $C=C—C=O$, the next ester to be studied was methyl α-phenylcinnamylidene-acetate, which differs from the malonate only in having the less negative phenyl group in the α position.

The results with this ester differ widely from those with the malonate and also from those with the corresponding benzylidene esters. Under conditions which are usually favorable for the reaction between Grignard's reagent and unsaturated esters, the reaction in this case does not take place at all or only to a very slight extent. When the ester is added to a large excess of the magnesium compound at the temperature of boiling ether, it is possible to bring about a reaction but the yield of product is never quantitative. The resulting compounds are not esters, formed by 1,4 addition, but ketones or tertiary alcohols formed by replacement of the methoxyl group and subsequent addition of a second molecule of reagent in the 1,4 or 1,2 position, according to the nature of the magnesium compound.

The reactions between phenylmagnesium bromide and the corresponding benzylidene and cinnamylidene esters are as follows:

1. $C_6H_5CH = C—COOR + C_6H_5MgBr =$
   $\qquad\qquad\quad |$
   $\qquad\qquad COOR$

$$C_6H_5CH—C = C\begin{array}{l}OMgBr[1]\\ \\OR\end{array} ;$$
$$\quad\ |\qquad\ |$$
$$\ C_6H_5\ \ COOR$$

2. $C_6H_5CH = CCOOR + C_6H_5MgBr =$
   $\qquad\qquad\ |$
   $\qquad\qquad C_6H_5$

$$C_6H_5CH—C = C\begin{array}{l}OMgBr[2]\\ \\OR\end{array} ;$$
$$\quad\ |\qquad\ |$$
$$\ C_6H_5\ \ C_6H_5$$
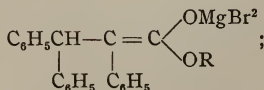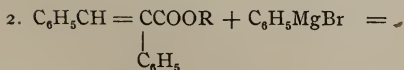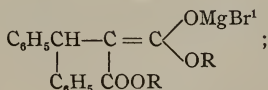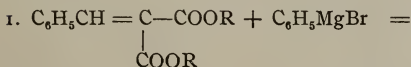
[1] Kohler: This Journal, **34**, 132.
[2] Kohler and Heritage: *Ibid.*, **33**, 153.

3. $C_6H_5CH = CHCH = \underset{\underset{COOR}{|}}{C}COOR + C_6H_5MgBr =$

$$C_6H_5CH = CHCH\underset{\underset{C_6H_5}{|}}{-}C = C\underset{OR}{\overset{OMgBr^1}{<}} \; ;$$

(with $\underset{C_6H_5}{|}$ and $\underset{COOR}{|}$ on the two central carbons)

4. $C_6H_5CH = CHCH = \underset{\underset{C_6H_5}{|}}{C}-COOR + 2C_6H_5MgBr =$

$$C_6H_5CH = CHCH\underset{\underset{C_6H_5}{|}}{-}C = C\underset{C_6H_5}{\overset{OMgBr}{<}} + MgORBr.$$

(with $\underset{C_6H_5}{|}$ on the central carbon)
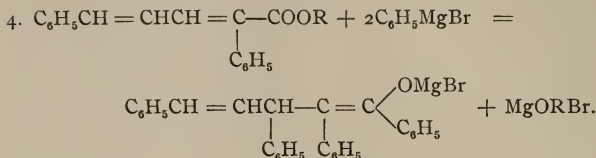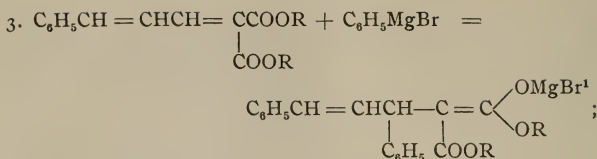
Of the above reactions the first three take place smoothly under a variety of conditions. The entire product is formed by 1,4 addition. The fourth reaction does not take place readily. The product consists of 87 per cent ketone, formed by replacement of the OR group and addition of a second molecule of the reagent in the 1,4 position to the ketone thus formed. In view of the similarity between reactions (1) and (2), it is not probable that the difference between reactions (3) and (4) is due entirely to the chemical nature of the α substituent.

A possible explanation for the great unreactivity of α-phenyl-cinnamylideneacetate may be found in a consideration of the spatial arrangement of the molecule. The possible configurations of the ester molecule are

I.   II.
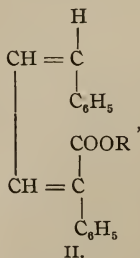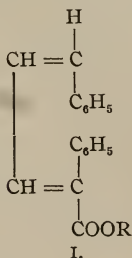
[1] *Loc. cit.*

and the two isomers in which the hydrogen of the benzal group is in the vicinity of the phenyl or the ester group. Of the compounds I. and II., the second would be more stable as the negative phenyl group is in the neighborhood of the more positive —COOCH$_3$ group.[1] If the molecule has this configuration, the ester group would be protected in a way analogous to that of a diortho substituted ester, as may be seen by the formula

$$\text{CH}$$
$$\text{HC} \quad \text{C}_6\text{H}_5$$
$$\text{HC}^4 \quad \overset{2\ 1}{\text{COOCH}_3}$$
$$\underset{3}{\text{C.C}_6\text{H}_5}$$
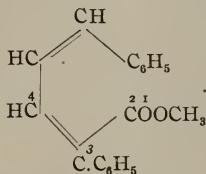
If the formula of this ester is compared with that of methyl cinnamylidenemalonate,

$$\text{CH}$$
$$\text{HC} \quad \text{C}_6\text{H}_5$$
$$\text{HC}^4 \quad \text{COOCH}_3'$$
$$\underset{3}{\text{C}}—\overset{2\ 1}{\text{COOCH}_3}$$
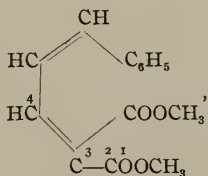
it is seen that the possibility of steric hindrance does not arise in the latter case. Only one of the ester groups enters into reaction and one of these is free to react, no matter what the spatial arrangement of the molecule is. Experiments have shown that there is, in fact, no hindrance, the reaction taking place smoothly at 0°.

A further substantiation of this view is found, in the case of the two isomeric methyl cinnamylideneacetates, in which hydrogen is present in place of the α-phenyl group. Preliminary experiments have shown that these esters react readily with Grignard's reagent at —15°.

It was also found that whereas methyl- and phenylmagnesium halides react with the α-phenyl ester under favorable

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[1] *Cf.* Stoermer and Frederici: Ber. d. chem. Ges., **41**, 324.

conditions, giving comparatively large yields, benzyl-magnesium bromide gives but a 17 per cent yield, and still larger molecules, such as naphthyl- and *o*-tolylmagnesium bromide, gave too small a quantity of reaction product to be isolated.

It is possible that, with the aromatic magnesium compounds, 1,4 addition to the ester in question takes place to a small extent, but the speed of the replacement reaction, under conditions which are necessary in order that a reaction may take place at all, is so much greater than that of the addition reaction that the final product is practically entirely ketone formed by replacement of the methoxyl group and subsequent addition of a second molecule of the reagent.

EXPERIMENTAL.

The α-phenylcinnamylideneacetic acid used was prepared by the method of Thiele.[1] It was found possible to purify the acid quickly and satisfactorily as follows: The crude acid was dissolved in a hot, concentrated solution of sodium carbonate from which, on cooling, the sodium salt separated in glistening yellow plates. The salt was filtered, dried, and then purified by being vigorously shaken with ether in a large flask. The ethereal extract contained hydrocarbon, formed by decomposition of part of the acid, and a very small quantity of sodium salt. The acid was precipitated from a concentrated solution of the purified salt. An 83 per cent yield of acid, pure after one crystallization from alcohol, was obtained.

The methyl ester was prepared according to the directions of Michael and Leighton.[2]

Reaction with Phenylmagnesium Bromide. α,β-*Diphenyl-γ-ben-zalbutyrophenone*, $C_6H_5CH = CHCH—CHCOC_6H_5$.—An ethereal

$$\overset{|}{C_6H_5} \overset{|}{C_6H_5}$$
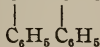
solution containing 7 grams (1 mol.) of phenylmagnesium bromide was slowly added to an ethereal solution of 14 grams (1 mol.) of the methyl ester cooled to —10°, and the mixture

[1] Ann. Chem. (Liebig), **306**, 197.
[2] J. prakt. Chem. [2], **68**, 521.

kept at that temperature for one hour. The product was treated with iced hydrochloric acid and the ethereal extract dried over calcium chloride. On evaporating, over 13 grams of the original ester crystallized out. There had been, therefore, practically no reaction.

The experiment was repeated at 0° with the same proportions of reagents and the mixture allowed to stand 15 hours at room temperature. Twelve and a half grams of ester were recovered.

When the proportions of ester to magnesium compound were 1 : 2 and the ester was added to the reagent a reaction took place at 0°, a very small quantity of a white crystalline solid separating from the ethereal solution after decomposition of the reaction product with ice and hydrochloric acid. This was subsequently proved to be a ketone formed by replacement of the methoxyl group and addition of a second molecule of reagent in the 1,4 position. After complete evaporation of the ether a brown, pasty mass remained. This was boiled with alcoholic potash for two hours, the alcohol evaporated, and the residue extracted repeatedly with water. From the aqueous solution hydrochloric acid precipitated an acid in a very impure condition. It was necessary to recrystallize this acid from alcohol and water a great many times before it was pure enough for identification. It was then found to be α-phenylcinnamylideneacetic acid, formed by hydrolysis of the original ester which had not entered into reaction with the Grignard's reagent. The fact that the acid was so extremely hard to purify makes it probable that a small quantity of some other acid, possibly formed by 1,4 addition to the ester, was present. No such compound could, however, be isolated.

The reaction was carried out in boiling benzene but the results were unsatisfactory.

The ketone mentioned above was the only product of reaction which could be isolated. To obtain the best yield of this compound the following procedure was adopted: An ethereal solution containing 1 molecule of ester was added very slowly to a boiling ethereal solution containing at least 3 molecules of phenylmagnesium bromide and the mixture boiled for two

hours. After decomposition in the usual way the ethereal extract was dried and the ether entirely evaporated. The oily product was suspended in alcohol, excess of alcoholic potash added, and the mixture boiled for one hour to remove any unchanged ester. The alcohol was then evaporated off, the solid residue extracted several times with water, and dried in a current of air. From the aqueous extract only a trace of original acid was obtained.

The solid product was purified by crystallization from a mixture of chloroform and alcohol. Analyses and subsequent reactions proved the substance to be α,β-diphenyl-γ-benzal-butyrophenone.

Analysis:

0.1508 gram substance gave 0.4966 gram CO_2 and 0.0877 gram H_2O.

	Calculated for $C_{29}H_{24}O$.	Found.
C	89.69	89.81
H	6.18	6.46

Molecular weight determined in boiling benzene. $K = 26.1$.

Weight solvent.	Weight substance.	Elevation of boiling point.	Molecular weight.
51.1100 grams	0.3764 gram	0°.050	384
	0.5700 "	0°.073	398
	0.6962 "	0°.093	382
		Average,	388
		Calculated,	388

The compound is readily soluble in acetone, chloroform, and benzene, fairly soluble in ligroin and boiling alcohol, very slightly soluble in ether, insoluble in water. It separates from a mixture of chloroform and alcohol in very fine, soft, white needles, melting at 191°.5–192°.5. The purest product is obtained by crystallization from boiling alcohol, but the process is tedious for purification of a large quantity, as a liter of boiling alcohol is necessary to dissolve five grams of ketone. The substance dissolves slowly in concentrated sulphuric acid from

which it may be precipitated by water. The solution in sulphuric acid is a pale, salmon pink in color.

α,β-Diphenyl-β-benzoylpropionic Acid,C_6H_5COCH—$CHCOOH.$
                                              | |
                                           C_6H_5 C_6H_5
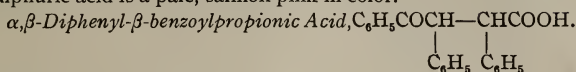
—This acid was obtained by oxidation of the ketone, thus proving the structure of the latter, the oxidation reaction taking place as follows:

$$C_6H_5CH = CHCH—CHCOC_6H_5 + 4O =$$
                   | |
                C_6H_5 C_6H_5

$$C_6H_5COOH + C_6H_5COCH—CHCOOH.$$
                            | |
                         C_6H_5 C_6H_5
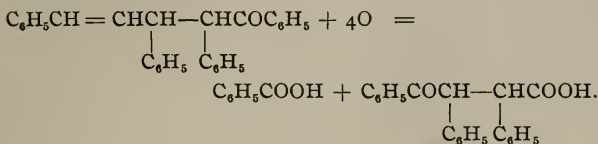
Twelve grams of ketone were dissolved in acetone, and finely powdered potassium permanganate was added gradually, the solution being kept cool by running water. Decolorization of the permanganate took place slowly. It was necessary to leave the mixture standing with excess of permanganate for several days, with frequent shaking, to insure complete oxidation. The solution was then decolorized by sulphur dioxide and filtered. The precipitated manganese dioxide was washed with acetone and then extracted repeatedly with boiling water. From the aqueous solution hydrochloric acid precipitated a colorless acid. This was crystallized from boiling alcohol from which it separates in small, shining needles melting at $211°$–$212°$. When dried on the water bath alcohol is given off and the crystals become opaque. The presence of alcohol of crystallization was proved by the formation of iodoform when the vapor from the heated acid was passed into a solution of potassium carbonate containing iodine.

Analysis of the air dried acid:

0.1539 gram substance gave 0.4517 gram CO_2 and 0.0768 gram H_2O.

	Calculated for $C_{22}H_{18}O_3.C_2H_5OH.$	Found.
C	80.00	80.04
H	5.45	5.54

0.3621 gram substance heated at 100° to constant weight lost 0.0444 gram.

Calculated for 1 mol. C_2H_5OH.	Found.
12.23	12.26

The acid is very readily soluble in chloroform, acetone, and ether, soluble in hot benzene and alcohol, slightly soluble in ligroin, insoluble in water. It dissolves readily in concentrated sulphuric acid. The color of the solution is at first a brilliant purple, changing during the course of half an hour to bright yellow and then to brown.

The aqueous filtrate from which this acid was precipitated was evaporated to small volume. On cooling, benzoic acid crystallized out.

From the acetone filtrate there was obtained by evaporation of the acetone a small quantity of a yellowish oil which partially solidified. The amount was too small for identification but the substance is possibly a decomposition product of the ketonic acid, as the yield of the latter was small. From 12 grams of ketone were obtained 5 grams of ketonic acid and 3.2 grams of benzoic acid, instead of the calculated 10.2 grams and 3.8 grams, respectively.

Methyl α,β-Diphenyl-β-benzoylpropionate,
$C_6H_5COCH—CHCOOCH_3$.—Three grams of acid, dried at 100°,
  $\quad\quad\quad\ \ |\quad\quad |$
  $\quad\quad\ C_6H_5\ C_6H_5$
were dissolved in methyl alcohol and hydrochloric acid gas passed into the warmed solution for two hours. On cooling the solution the ester crystallized out in shining, stiff, white needles. After one crystallization from methyl alcohol it melted sharply at 159°.

Analysis:

0.1508 gram substance gave 0.4418 gram CO_2 and 0.0818 gram H_2O.

	Calculated for $C_{22}H_{20}O_2$.	Found.
C	80.23	79.90
H	5.81	6.02

The ester is readily soluble in ether, alcohol, chloroform, and acetone, slightly soluble in boiling ligroin, insoluble in cold ligroin and water. It dissolves slowly in concentrated sulphuric acid. The solution has the same purple color as that of the ketonic acid and the colors change in the same way.

α,β-Diphenyl-γ-benzalbutyrophenone forms no oxime nor hydrazone. Five grams of the ketone in alcoholic solution were boiled with excess of potassium hydroxide and hydroxylamine hydrochloride for ten hours. The entire amount of ketone was regained unchanged. In this respect the ketone resembles benzpinacoline[1] and other ketones in which the reactivity of the carbonyl oxygen is hindered by the groups in its immediate vicinity.

The same hindrance effect was noted when the ketone was treated with phenylhydrazine. No hydrazone was formed. This behavior is in accordance with the results obtained by Petrenko-Kritschenko and Eltschaninoff[2] and other investigators.

The ketone reacts readily, however, with Grignard's reagent. Thirteen and a half grams of ketone, suspended in absolute ether, were added slowly to a solution of phenylmagnesium bromide which contained 3 molecules of reagent for 1 of ketone. The reaction took place readily at 0° but, because of the relative insolubility of the ketone in ether, the reaction was usually carried out in boiling solution. After all the ketone had been added, the clear, rose colored solution was boiled for an hour and then decomposed in the usual way. After evaporation of the ether a heavy yellow oil remained. This was suspended in water and distilled with steam to remove a small quantity of diphenyl. The oil remaining in the flask could not be made to solidify under a variety of conditions. It decomposed when distilled under diminished pressure so that it was not possible to obtain it in pure condition. It was, therefore, oxidized The oil was dissolved in acetone and treated with powdered potassium permanganate. The

Beckmann: Ann. Chem. (Liebig), **252**, 14.
Ann. Chem. (Liebig), **341**, 150.

reduction of the permanganate took place rapidly with considerable evolution of heat. The excess of permanganate was reduced with sulphur dioxide, and the precipitated manganese dioxide washed carefully with hot acetone. From the acetone solution a white, crystalline solid separated. It was purified by recrystallization from hot alcohol, from which it separates in fine needles, melting at 221°–221°.5. Analyses and reactions show that the substance is a lactone formed by the loss of a molecule of water from the γ-oxy acid which results from the oxidation of the tertiary alcohol formed by the reaction of phenylmagnesium bromide on the ketone.

$$C_6H_5CH = CHCH{-}\underset{\underset{C_6H_5}{|}}{CH}\underset{\underset{C_6H_5}{|}}{CO}C_6H_5 + C_6H_5MgBr \longrightarrow$$

$$C_6H_5CH = CHCH{-}\underset{\underset{C_6H_5}{|}}{CH}{-}\underset{\underset{OH}{|}}{C}(C_6H_5)_2 ;$$

$$C_6H_5CH = CHCH{-}\underset{\underset{C_6H_5}{|}}{CH}{-}\underset{\underset{OH}{|}}{C}(C_6H_5)_2 + 4O \longrightarrow$$

$$C_6H_5COOH + (C_6H_5)_2\overset{\overline{\qquad\qquad}O}{C}{-}\underset{\underset{C_6H_5}{|}}{CH}{-}\underset{\underset{C_6H_5}{|}}{CH}{-}CO + H_2O.$$

Analyses:

I. 0.1492 gram substance gave 0.4721 gram CO_2 and 0.0811 gram H_2O.

II. 0.1487 gram substance gave 0.4690 gram CO_2 and 0.0815 gram H_2O.

	Calculated for $C_{28}H_{22}O_2$.	I.	Found. II.
C	86.15	86.29	86.02
H	5.64	6.03	6.08

The lactone of γ-oxytetraphenylbutyric acid is soluble in ether, acetone, and chloroform, fairly soluble in hot benzene, ligroin, and alcohol. It is not affected by sodium carbonate solution but after long boiling in aqueous alcohol

which contains excess of potassium hydroxide it partially dissolves. When the alcohol is evaporated off and the aqueous solution acidified the lactone is precipitated.

The manganese dioxide precipitated during the oxidation was extracted with boiling water, and the filtrates concentrated by evaporation and acidified. A colorless acid was precipitated which, after one crystallization from water, melted sharply at 121°. It was pure benzoic acid.

A small quantity of a yellow oil was left after complete evaporation of the acetone from which the lactone had separated. It has a pleasant aromatic odor resembling that of diphenylmethane. The amount of the substance was too small to admit of purification and identification.

It is probable that the oil obtained as the product of the reaction between phenylmagnesium bromide and diphenylbenzalbutyrophenone is a mixture of a tertiary alcohol and its decomposition products, as it is to be expected that a substance of the composition of this alcohol would be a solid. When distilled under diminished pressure no water was given off and no constant boiling substance obtained. The distillate was a yellow oil from which crystals gradually separated. The substance was recrystallized from ligroin from which it separated in needles melting at 134°–135°.

Analyses:

I. 0.1226 gram substance gave 0.3962 gram CO_2 and 0.0692 gram H_2O.

II. 0.1532 gram substance gave 0.4941 gram CO_2 and and 0.0836 gram H_2O.

	Calculated for $C_{22}H_{18}O$.	I.	Found. II.
C	88.59	88.13	87.96
H	6.04	6.27	6.06

The substance is readily soluble in benzene, chloroform, and alcohol, fairly soluble in ether and ligroin. It is unsaturated as it at once decolorizes a solution of potassium permanganate in the cold. Since benzoic acid is one of the products of oxidation the substance contains the group

$C_6H_5CH = CH$. No other acid product of oxidation was obtained.

A small quantity of a yellowish oil was left after separation of the crystals from the distillate. This had a strong odor of diphenylmethane but was too small in quantity and too impure to be identified.

It is probable that the tertiary alcohol decomposes to a slight extent on formation and completely on distillation in the following way:

$$C_6H_5CH = CHCH—CH—C(C_6H_5)_2 \ \longrightarrow$$
$$\underset{\displaystyle C_6H_5 \ \ C_6H_5 \ \ OH}{|\qquad |\qquad |}$$

$$C_6H_5CH = CHCHCOC_6H_5 + (C_6H_5)_2CH_2.$$
$$\underset{\displaystyle C_6H_5}{|}$$
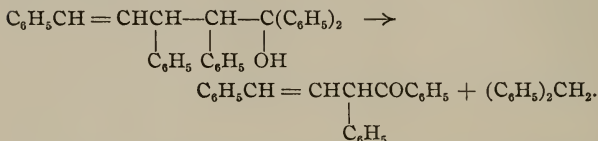
This ketone, phenylbenzalpropiophenone, has the composition $C_{22}H_{18}O$ and would give benzoic acid on oxidation. The other oxidation product, phenylbenzoylacetic acid, spontaneously decomposes so that no other acid product of oxidation would be obtained.

Brom-α,β-diphenyl-γ-benzalbutyrophenone,
$$C_6H_5CBr = CHCH—CHCOC_6H_5 \quad \text{or}$$
$$\underset{\displaystyle C_6H_5 \ \ C_6H_5}{|\qquad |}$$

$$C_6H_5CH = CBrCH—CHCOC_6H_5.$$
$$\underset{\displaystyle C_6H_5 \ \ C_6H_5}{|\qquad |}$$
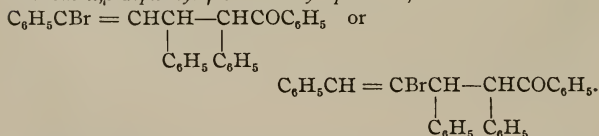
—Three grams of diphenylbenzalbutyrophenone were dissolved in chloroform and one molecule of bromine in chloroform solution was added slowly. The temperature of the solution was kept at 0°. The bromine solution was decolorized as fast as added and fumes of hydrobromic acid were given off as soon as the reaction began. After all the bromine had been added, the chloroform was allowed to evaporate spontaneously. The colorless, crystalline product remaining was recrystallized from a mixture of chloroform and alcohol. After several recrystallizations, analyses showed that the substance was a mixture of a mono- and a dibrom-

ketone. It was, therefore, dissolved in chloroform and heated for some time on the water bath to decompose the dibrom compound. The product, on crystallization from chloroform and alcohol, separated in firm, white needles melting at 186°–187°.

Analysis:

0.1536 gram substance gave 0.4201 gram CO_2 and 0.0711 gram H_2O.

	Calculated for $C_{29}H_{23}OBr$.	Found.
C	74.50	74.57
H	4.92	5.14

The compound is readily soluble in benzene, acetone, chloroform, and ether, slightly soluble in alcohol, insoluble in water.

Attempts were made to determine the structure of the compound by oxidation. When the reaction was carried out under the conditions which are necessary for the oxidation of the original ketone the whole amount of the bromine compound was regained unchanged. When the mixture of bromine compound and excess of potassium permanganate in acetone solution was left standing ten days with frequent shaking, oxidation took place to a small extent. Some benzoic acid was obtained but a large part of the bromketone was regained. The great difference between the reactivity of the original ketone and the bromketone toward the oxidizing agent indicates that the bromine is attached to a doubly linked carbon atom. The fact that no odor of benzaldehyde was noticed during oxidation would point to the first rather than to the second formula given.

Reaction with Benzylmagnesium Bromide. α-Phenyl-β-benzyl-γ-benzalpropylbenzyl Ketone, $C_6H_5CH=CHCH\underset{\underset{CH_2C_6H_5C_6H_5}{|}}{——}CHCOCH_2C_6H_5$.

—The reaction was carried out under the conditions which gave the best yield of reaction product with phenylmagnesium bromide. Fifteen grams of ester were used. The oily product was suspended in water and distilled with steam to remove dibenzyl. The oil was then dissolved in alcohol and

boiled with excess of alcoholic potash for two hours to saponify any unchanged ester. From the aqueous extract of the product, hydrochloric acid precipitated ten grams of crude α-phenylcinnamylideneacetic acid. The residue, insoluble in water, was dissolved in hot alcohol from which it crystallized, on cooling, in fine white needles melting at $150°$.

Analysis:

0.1229 gram substance gave 0.4025 gram CO_2 and 0.0780 gram H_2O.

	Calculated for $C_{21}H_{28}O$.	Found.
C	89.42	89.31
H	6.73	7.05

The substance is very soluble in ether, chloroform, benzene, and ligroin, fairly soluble in alcohol, insoluble in water. It dissolves readily in concentrated sulphuric acid. The solution is a brilliant crimson color.

But 4 grams of crude ketone were obtained from 15 grams of ester, a 17 per cent yield.

Reaction with Orthotolylmagnesium Bromide.—The reaction was carried out as with the other reagents. From 15 grams of ester 10 grams of the corresponding acid were regained and 65 per cent of the orthotolylmagnesium bromide was regained as toluene. A small quantity of an oily substance was the only product of the reaction. From this no pure substance could be obtained.

Reaction with Naphthylmagnesium Bromide.—The reaction was carried out as before. From 20 grams of ester used 10 grams of acid were regained and 50 per cent of the naphthylmagnesium bromide was regained as naphthalene. As in the preceding case, no pure product could be obtained from the tarry substance formed, in small quantity, as a product of the reaction.

Reaction with Methylmagnesium Iodide.—When methylmagnesium iodide in ethereal solution was added to a solution of the ester in the same solvent, in a freezing mixture, at room temperature, or at the temperature of boiling ether, the whole amount of ester was regained. A reaction took place only

when excess of methylmagnesium iodide was present, the ester added to a solution of the reagent in boiling ether, and the reaction mixture boiled for some time.

Twenty-five grams of ester, dissolved in ether, were added slowly to a boiling solution containing 4 molecules of the reagent to 1 of ester. The solution was boiled for 10 hours and allowed to stand at room temperature for the same length of time. After decomposition of the magnesium compound and evaporation of the ether, the oily product was boiled for two hours with alcoholic potash. Less than 2 grams of crude acid, formed by saponification of unused ester, were obtained. The product of the reaction was a heavy reddish oil which could not be made to solidify. It was carefully washed, dried, and analyzed.

Analysis:

0.1918 gram substance gave 0.6368 gram CO_2 and 0.1325 gram H_2O.

	Calculated for $C_{19}H_{20}O$.	$C_{19}H_{18}$.	Found.
C	86.36	92.68	90.54
H	7.57	7.31	7.66

As the analysis gave results too high in carbon for a ketone or tertiary alcohol, it seemed probable that the compound was a mixture of tertiary alcohol and a hydrocarbon formed by loss of water from the alcohol. The presence of the hydroxyl group was proven by treating a solution of the oil with methylmagnesium iodide. There was a steady evolution of methane.

The oil was then distilled under diminished pressure. Water was split off and a yellow oil distilled over at 140°–150° (25 mm.). This oil was redistilled. From the distillate colorless, compact crystals gradually separated. These were washed with alcohol and crystallized from glacial acetic acid. From this solvent the compound separates in firm, white crystals, melting at 97°–98°.

Analysis:

0.1027 gram substance gave 0.3471 gram CO_2 and 0.0700 gram H_2O.

	Calculated for $C_{19}H_{18}$.	Found.
C	92.68	92.17
H	7.31	7.57

The hydrocarbon dissolves readily in ether, chloroform, acetone, and benzene, is moderately soluble in ligroin and glacial acetic acid, almost insoluble in cold alcohol, fairly soluble in hot alcohol, from which it separates in an oily condition.

The first product of the reaction is undoubtedly a ketone formed by replacement of the methoxyl group as in the reactions with phenyl- and benzylmagnesium halides. The ketone thus formed at once reacts with a second molecule of methylmagnesium iodide, the addition being to the carbonyl group, the usual reaction with methyl ketones. The tertiary alcohol thus formed easily loses water to form the unsaturated hydrocarbon:

$$C_6H_5CH = CHCH = CCOOCH_3 \longrightarrow$$
$$\underset{C_6H_5}{|}$$

$$[C_6H_5CH = CHCH = CCOCH_3] \longrightarrow$$
$$\underset{C_6H_5}{|}$$

$$C_6H_5CH = CHCH = C-C(CH_3)_2OH \longrightarrow$$
$$\underset{C_6H_5}{|}$$

$$H_2O + C_6H_5CH = CHCH = C-C = CH_2.$$
$$\underset{C_6H_5}{|} \quad \underset{CH_3}{|}$$
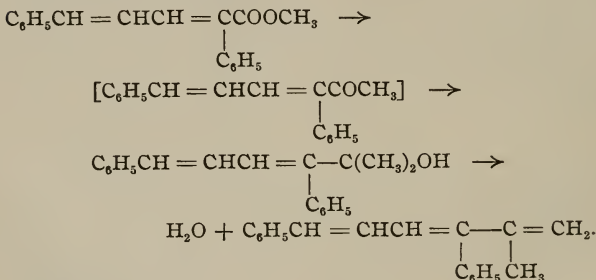
Chemical Laboratory,
Barnard College,
July, 1908.

CLXI.—RESEARCHES ON PYRIMIDINES: SYNTHESES OF SOME BENZYL DERIVATIVES OF URACIL AND THYMINE.

[THIRTY-EIGHTH PAPER.]

By Treat B. Johnson and John H. Derby, Jr.

In order to determine the structure of some new nitrogen derivatives of uracil and thymine it was essential to have knowledge of some characteristic nitrogen-alkyl derivatives of

these pyrimidines of known constitution. The only nitrogen-alkyl derivatives of uracil and thymine mentioned in the literature are 1,3-dimethylthymine[1] and the methyl and ethyl compounds, which have been described in previous papers from this laboratory.[2] These alkyl pyrimidines were not suitable for our work on account of their solubility, and difficulty of isolation when accompanied by impurities. Furthermore, 3-methyluracil has not been synthesized.

With the anticipation that the nitrogen-benzyl derivatives of uracil and thymine might be found to be more insoluble, and suitable for our work, we undertook this investigation. We shall describe in this paper the methods of preparation and the properties of 1-benzyluracil, I., 3-benzyluracil, II., 1-benzylthymine, III., and 3-benzylthymine, IV.

$$
\begin{array}{ll}
\mathrm{C_6H_5CH_2N\!\!-\!\!-\!\!-\!\!CO} & \mathrm{NH\!\!-\!\!-\!\!-\!\!CO} \\
\quad\;\; | \qquad\qquad | & \qquad | \qquad\qquad | \\
\quad\;\;\mathrm{CO} \qquad \mathrm{CH} & \qquad \mathrm{CO} \qquad \mathrm{CH} \\
\quad\;\; | \qquad\qquad \| & \qquad | \qquad\qquad \| \\
\quad\;\;\mathrm{NH\!\!-\!\!CH} & \mathrm{C_6H_5CH_2N\!\!-\!\!-\!\!-\!\!CH} \\
\qquad\quad \mathrm{I.} & \qquad\qquad\quad \mathrm{II.}
\end{array}
$$

$$
\begin{array}{ll}
\mathrm{C_6H_5CH_2N\!\!-\!\!-\!\!-\!\!CO} & \mathrm{NH\!\!-\!\!-\!\!CO} \\
\quad\;\; | \qquad\qquad | & \qquad | \qquad\qquad | \\
\quad\;\;\mathrm{CO} \qquad \mathrm{CCH_3} & \qquad \mathrm{CO} \qquad \mathrm{CCH_3} \\
\quad\;\; | \qquad\qquad \| & \qquad | \qquad\qquad \| \\
\quad\;\;\mathrm{NH\!\!-\!\!-\!\!CH} & \mathrm{C_6H_5CH_2N\!\!-\!\!-\!\!-\!\!CH} \\
\qquad\quad \mathrm{III.} & \qquad\qquad\quad \mathrm{IV.}
\end{array}
$$
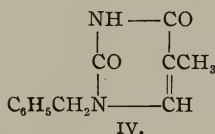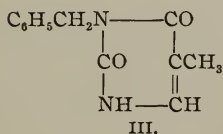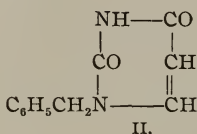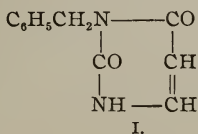
Johnson and Heyl[3] showed that methyl iodide reacts with 2-ethylmercapto-6-oxypyrimidine,[4] in presence of alkali, giving 1-methyl-2-ethylmercapto-6-oxypyrimidine, V. They did not observe the formation of the isomeric 2-ethylmercapto-3-methyl-6-oxypyrimidine, VI. Wheeler and Liddle[5] observed, on the other hand, that ethyl chloracetate reacts with this mercaptopyrimidine, giving 2-ethylmercapto-3-ethylacetate-6-

[1] Steudel: Z. physiol. Chem., **30**, 539.

[2] Johnson and Heyl: This Journal, **37**, 628; Johnson and Clapp: J. Biol. Chem. **5**, 49.

[3] *Loc. cit.*

[4] This Journal, **29**, 478, 492.

[5] J. Am. Chem. Soc., **30**, 1152.

oxypyrimidine, VII., instead of the isomeric mercaptopyrimidine, VIII.

```
CH₃N————CO              N————CO
    |      |            ||     |
C₂H₅SC    CH       C₂H₅SC     CH
    ||     ||           |      ||
    N————CH         CH₃N————CH
      V.                   VI.

C₂H₅O₂C.CH₂N————CO          N————CO
        |        |          ||     |
   C₂H₅SC       CH     C₂H₅SC      CH
        ||       ||         |       ||
        N————CH    C₂H₅O₂C.CH₂N————CH
         VIII.                  VII.
```
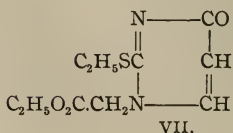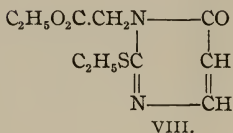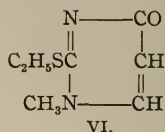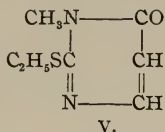
We now find that benzyl chloride reacts with 2-ethylmercapto-6-oxypyrimidine in presence of alkali, giving a mixture of two isomeric mercaptopyrimidines melting at 77° and 139.° They were converted quantitatively into the corresponding benzyluracils melting at 175° and 173°, respectively, by hydrolysis with hydrochloric acid.

The structures of the benzyluracils and incidentally of the mercaptopyrimidines were established in the following manner: The benzyluracil melting at 173° reacted with methyl iodide, giving 1-methyl-3-benzyluracil, XVI. This same pyrimidine was also obtained by the action of benzyl chloride on 1-methyl-uracil,[1] XVIII. This benzyl derivative is therefore to be represented as 3-benzyluracil, XIII., and the isomer, melting at 175°, as 1-benzyluracil, XII. The mercaptopyrimidines, melting at 77° and 139°, are therefore to be assigned the structural formulas IX. and X., *viz.*, 1-benzyl-2-ethylmercapto-6-oxypyrimidine and 2-ethylmercapto-3-benzyl-6-oxypyrimidine, since they are converted into 1-benzyluracil, XII., and 3-benzyluracil, XIII., respectively, by hydrolysis with acids.

2-Ethylmercapto-5-brom-6-oxypyrimidine[2] reacted with benzyl chloride, giving an excellent yield of 2-ethylmercapto-3-benzyl-5-brom-6-oxypyrimidine, XI. This was converted

[1] Johnson and Heyl: *Loc. cit.*
[2] This Journal, **31**, 603.

quantitatively into 3-benzyl-5-bromuracil, XIV., by hydrolysis with hydrochloric acid. The same pyrimidine was also formed by the action of bromine on 3-benzyluracil, XIII. 1-Methyl-3-benzyl-5-bromuracil, XVII., was formed by treatment of 3-benzyl-5-bromuracil, XIV., with methyl iodide, in presence of alkali, and also by the action of bromine on 1-methyl-3-benzyluracil, XVI.

3-Benzyluracil, XIII., reacted with cold, fuming nitric acid, giving a dinitropyrimidine which we have provisionally represented as 3-*p*-nitrobenzyl-5-nitrouracil, XV.

Johnson and Clapp[1] observed that 2-ethylmercapto-5-methyl-6-oxypyrimidine, XIX., reacted with methyl iodide, in presence of alkali, giving about equal proportions of 1,5-dimethyl-2-ethylmercapto-6-oxypyrimidine, XX., and 2-ethyl-mercapto-3,5-dimethyl-6-oxypyrimidine, XXI. We now find that benzyl chloride reacts with this mercaptopyrimidine, under the same conditions, giving 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine, XXII., melting at 72°, and 2-ethylmercapto-3-benzyl-5-methyl-6-oxypyrimidine, XXIV., melting at 121°–122°. These pyrimidines were converted quantitatively into 1-benzylthymine, XXIII., melting at 205°, and 3-benzyl-thymine, XXVI., melting at 159°–160°, by hydrolysis with concentrated hydrochloric acid.

The structures of these four pyrimidines was determined by the behavior of the two benzylthymines towards diazobenzene-sulphonic acid. Johnson and Clapp[2] have shown in a recent paper that this reagent can be used to distinguish between 1- and 3-alkyl derivatives of uracil and thymine. They observed, for example, that 1-alkyl derivatives of these pyrimidines reacted with this reagent, giving red colored solutions. The isomeric 3-alkylpyrimidines, on the other hand, did not react with the diazo acid with the formation of red colors. We now find that the benzylthymine, melting at 205°, reacts with the sulphonic acid, giving a brilliant red solution, indicating that it is a 1-benzylthymine as represented by formula XXIII. The isomer gave no color with the sulphonic acid and therefore

[1] *Loc. cit.*
[2] J. Biol. Chem., Vol. **5.**

Reaction scheme (rotated 90° on the page):

Starting compound:
```
NH——CO
|     \
C2H5SC CH
‖      ‖
N======CH
```

→ **X.**
```
N======CO——CH
|          ‖
C2H5SC     CH
|
C6H5CH2N————
```

→ **XIII.**
```
NH——CO——CH
|        ‖
CO       CH
|
C6H5CH2N————
```

→ **XVI.**
```
CH3N——CO——CH
|         ‖
CO        CH
|
C6H5CH2N————
```

XVIII.
```
CH3N——CO——CH
|         ‖
CO        CH
|
NH————CH
```

Upper row:

XI.
```
N======CO——CBr
|          ‖
C2H5SC     CH
|
C6H5CH2N————
```

→ **XIV.**
```
NH——CO——CBr
|        ‖
CO       CH
|
C6H5CH2N————
```

→ **XVII.**
```
CH3N——CO——CBr
|         ‖
CO        CH
|
C6H5CH2N————
```

Lower row:

IX.
```
C6H5CH2N——CO——CH
|             ‖
C2H5SC        CH
‖
N=============CH
```

→ **XII.**
```
C6H5CH2N——CO——CH
|             ‖
CO            CH
|
NH————————————CH
```

XV.
```
NH——CO——CNO2
|        ‖
CO       CH
|
NO2C6H4CH2N——
```

N——CO
∥   ∣
C₂H₅S·C   CCH₃
∥   ∥
CH₃N——CH

XXI.

N——CO
∥   ∣
C₂H₅SC   CCH₃
∥   ∥
C₆H₅CH₂N——CH

XXIV.

CH₃N——CO
∣   ∣
CO   CCH₃
∣   ∥
C₆H₅CH₂N——CH

XXVII.

NH——CO
∣   ∣
C₂H₅SC   CCH₃
∥   ∥
N——CH

XIX.

C₆H₅CH₂N——CO
∣   ∣
CO   CCH₃
∣   ∥
NH——CH

XXIII.

NH——CO
∣   ∣
CO   CCH₃
∣   ∥
C₆H₅CH₂N——CH

XXVI.

CH₃N——CO
∣   ∣
C₂H₅SC   CCH₃
∥   ∥
N——CH

XX.

C₆H₅CH₂N——CO
∣   ∣
C₂H₅SC   CCH₃
∥   ∥
N——CH

XXII.

NH——CO   CH₃
∣   C⟨ NO₂
CO   CHOH
∣
NO₂C₆H₄CH₂N

XXV.

is to be assigned formula XXVI. The corresponding mercaptopyrimidines melting at 72° and 121°–122° must therefore be represented by formulas XXII. and XXIV., respectively.

It is of interest to note here that the structures of the above benzyluracils, XII. and XIII., can also be determined by means of the diazo reagent. 1-Benzyluracil, XII., reacted with the acid, in presence of sodium hydroxide, giving a permanent red color, while its isomer, XIII., did not give a red color under the same conditions.

1-Methyl-3-benzylthymine, XXVII., was formed by the action of methyl iodide on 3-benzylthymine, XXVI. When the latter pyrimidine, XXVI., was dissolved in cold, fuming nitric acid of density 1.5 it was converted into a hydropyrimidine,[1] XXV., *viz.*, 3-*p*-nitrobenzyloxynitrohydrothymine.

The four pyrimidines, 1-benzyluracil, 3-benzyluracil, 1-benzylthymine, and 3-benzylthymine, are characterized by their insolubility in cold water. 3-Benzyluracil and 3-benzylthymine are less soluble in water than uracil and thymine. They all crystallize from hot water without water of crystallization. They are weak acids and can be heated above their melting points without decomposition.

<div align="center">EXPERIMENTAL PART.</div>

1-Benzyl-2-ethylmercapto-6-oxypyrimidine,

$$\begin{array}{cc} C_6H_5CH_2N\!\!-\!\!-\!\!CO \\ | \qquad\quad | \\ C_2H_5SC \qquad CH \\ \| \qquad\quad \| \\ N\!\!-\!\!-\!\!CH \end{array}$$
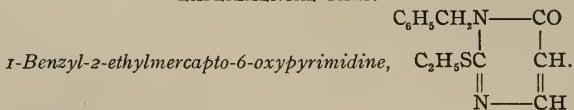
—Fifteen grams of 2-ethylmercapto-6-oxypyrimidine and 5.4 grams of finely pulverized potassium hydroxide were dissolved in about 75 cc. of boiling absolute alcohol. Twelve and two-tenths grams of benzyl chloride were then added and the solution heated on the steam bath until it gave no alkaline reaction with moist turmeric paper (about 4 hours). After cooling, the undissolved potassium chloride was filtered off and the alcohol removed by evaporation on the steam bath. We obtained a crystalline product which was triturated with 50 cc. of a 5 per cent solution of sodium hydroxide to remove un-

[1] Johnson: THIS JOURNAL, **40**, 19; J. Biol. Chem., **4**, 407.

altered pyrimidine and potassium chloride. When the alkaline solution was acidified with acetic acid we recovered 1.7 grams of 2-ethylmercapto-6-oxypyrimidine. The crystalline material, insoluble in sodium hydroxide, was then extracted thoroughly with an excess of ether and the insoluble material saved (see 3-benzyl derivative below). When the ether solution was allowed to evaporate we obtained some oil and about 3.0 grams of crystalline material which melted at 65°–70° to a clear oil with no effervescence. The oil gradually assumed a crystalline form on standing. The pyrimidine separated from alcohol in well-developed prisms melting at 77°. The weight of one crystal, which was selected for analysis, was 0.3+ gram. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}ON_2S$.	Found.
N	11.38	11.63

2-Ethylmercapto-3-benzyl-6-oxypyrimidine,

$$\begin{array}{ccc} & N\!\!-\!\!-\!\!-\!\!-CO & \\ & \| & | \\ C_2H_5SC & & CH. \\ & | & \| \\ C_6H_5CH_2.N\!\!-\!\!-\!\!-\!\!CH & \end{array}$$
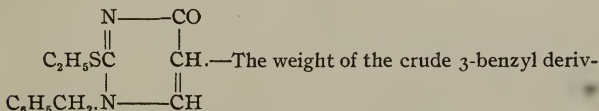
—The weight of the crude 3-benzyl derivative, insoluble in ether, in the above experiment, was 11.1 grams, corresponding to 51 per cent of the calculated. The pyrimidine is soluble in warm benzene, acetone, alcohol, very soluble in chloroform, and practically insoluble in cold ether and ligroin. It is difficultly soluble in hot water and crystallizes in long, slender prisms, and hexagonal prisms or flat tables melting at 139° to an oil. This melting point was not raised by recrystallization from benzene.

Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}ON_2S$.	Found. I.	II.
N	11.38	11.58	11.61

2-Ethylmercapto-3-benzyl-5-brom-6-oxypyrimidine,

$$\begin{array}{ccc} & N\!\!-\!\!-\!\!-\!\!-CO & \\ & \| & | \\ C_2H_5S.C & & CBr. \\ & | & \| \\ C_6H_5CH_2N\!\!-\!\!-\!\!-\!\!CH & \end{array}$$
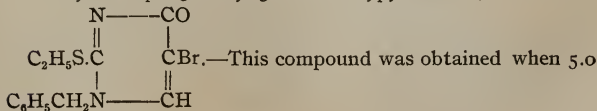
—This compound was obtained when 5.0

grams of 2-ethylmercapto-5-brom-6-oxypyrimidine[1] were heated in absolute alcohol, for 4 to 5 hours, with the required proportions of potassium hydroxide and benzyl chloride. After filtration from the undissolved potassium chloride and evaporation of the alcohol we obtained a semisolid substance which immediately solidified when washed with ether. The yield was 4.2 grams, corresponding to 60.0 per cent of the calculated. The pyrimidine is difficultly soluble in water and separates from a hot, aqueous solution in needles melting at 129° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{13}ON_2BrS$.	Found.
N	8.62	9.0

1-Benzyluracil,

$$C_6H_5CH_2.N\underset{\underset{NH}{|}}{\overset{\overset{CO}{|}}{}}\quad \underset{\underset{CH}{\|}}{\overset{\overset{CH}{|}}{}}$$

—A quantitative yield of this pyrimidine was obtained when 3.0 grams of the corresponding 2-mercaptopyrimidine were dissolved in 150 cc. of concentrated hydrochloric acid and the solution evaporated to dryness. It crystallizes from hot water in prismatic crystals melting at 175° to a clear oil. It did not contain water of crystallization. When mixed with the isomeric 3-benzyluracil (see below) melting at 173°, the fusion point was lowered to 140°–155°. The pyrimidine reacted with diazobenzenesulphonic acid, in presence of alkali, giving a red colored solution. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}O_2N_2$.	Found.
N	13.86	14.1

3-Benzyluracil,

$$\overset{\overset{NH}{|}}{}\quad \overset{\overset{CO}{|}}{}$$

—This pyrimidine was prepared by digesting 6.7 grams of 2-ethylmercapto-3-benzyl-6-oxypyrimidine with concentrated hydrochloric acid for 5 to 6

---

[1] Wheeler and Johnson: THIS JOURNAL, **31**, 603.

hours.   The yield was 5.5 grams or 96 per cent of the theoretical.
It crystallizes from alcohol in stout prisms melting at 173° to
a clear oil with no effervescence.   It is difficultly soluble in
water and moderately soluble in cold acetone; insoluble in cold
benzene and ether; and difficultly soluble in chloroform.   It
was insoluble in cold 25 per cent hydrochloric and sulphuric
acids and easily soluble in warm glacial acetic acid.   Analysis
(Kjeldahl):

	Calculated for $C_{11}H_{10}O_2N_2$	Found.	
		I.	II.
N	13.86	13.9	14.0

This pyrimidine does not react with diazobenzenesulphonic
acid to give a red colored solution.   The mixture assumed a
yellow color, which was permanent for 30 minutes.

Solubility of 3-Benzyluracil in Water.—One hundred parts
of water dissolved at 25°

I.	II.
0.0998 gram.	0.1008 gram.

3-Benzyl-5-bromuracil,

$$
\begin{array}{ccc}
\text{NH} & \!\!-\!\!\!- & \text{CO} \\
| & & | \\
\text{CO} & & \text{CBr.} \\
| & & \| \\
\text{C}_6\text{H}_5\text{CH}_2.\text{N} & \!\!-\!\!\!- & \text{CH}
\end{array}
$$
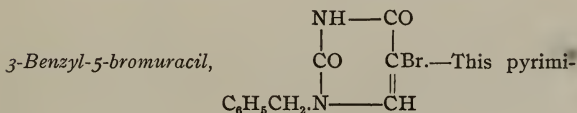
—This pyrimi-
dine can be prepared by treating 3-benzyluracil in glacial acetic
acid with the calculated quantity of bromine.   It crystallizes from
acetic acid in hexagonal prisms melting at 204° to a clear oil.
The same brompyrimidine was also prepared by dissolving
0.5 gram of 3-benzyluracil in bromine water and allowing the
solution to evaporate to dryness.   The residue, about 0.8–0.9
gram, was then digested with absolute alcohol for 2 hours
and the solution evaporated to dryness.   The compound
obtained by this treatment crystallized from alcohol in prisms
melting at 204°.   A quantitative yield of the pyrimidine was
also obtained by digesting 2-ethylmercapto-3-benzyl-5-brom-
6-oxypyrimidine with concentrated hydrochloric acid.   Anal-
ysis (Kjeldahl):

	Calculated for $C_{11}H_9O_2N_2Br.$	Found.
N	9.96	10.0

3-p-*Nitrobenzyl-5-nitrouracil*,

$$\begin{array}{ccc} NH & \!\!-\!\!-\!\! & CO \\ | & & | \\ CO & & CNO_2.- \\ | & & \| \\ NO_2.C_6H_4CH_2.N & \!\!-\!\!-\!\! & CH \end{array}$$
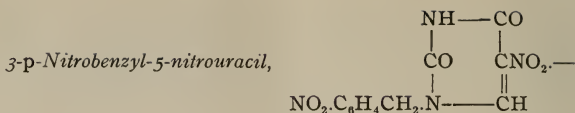
Five-tenths of a gram of 3-benzyluracil was dissolved, at ordinary temperature, in 10 cc. of fuming nitric acid of density 1.5. The acid solution was then allowed to stand at ordinary temperature when prismatic crystals separated. They were purified for analysis by recrystallization from hot water. The pyrimidine is difficultly soluble and separates in slender prisms, which decompose, according to the rate of heating, at 235°–240° with effervescence. Analysis (Kjeldahl):

	Calculated for		Found.	
	$C_{11}H_8O_6N_4$.	$C_{11}H_9O_4N_3$.	I.	II.
N	19.18	17.00	19.48	19.39

1-*Methyl-3-benzyluracil*,

$$\begin{array}{ccc} CH_3N & \!\!-\!\!-\!\! & CO \\ | & & | \\ CO & & CH.- \\ | & & \| \\ C_6H_5.CH_2N & \!\!-\!\!-\!\! & CH \end{array}$$
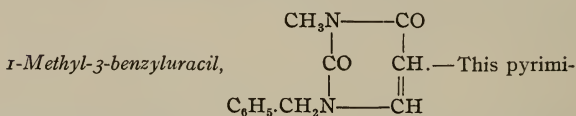
This pyrimidine is easily prepared by dissolving 3-benzyluracil and one molecular proportion of potassium hydroxide in alcohol and then warming with an excess of methyl iodide. The same pyrimidine was also obtained when 1-methyluracil[1] was digested in alcohol with the calculated proportions of potassium hydroxide and benzyl chloride. The pyrimidine is extremely soluble in alcohol and benzene. It crystallizes from dilute alcohol in needles melting at 75° to an oil without effervescence. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2$.	Found.	
		I.	II.
N	12.96	13.17	13.12

1-*Methyl-3-benzyl-5-bromuracil*,

$$\begin{array}{ccc} CH_3N & \!\!-\!\!-\!\! & CO \\ | & & | \\ CO & & CBr.- \\ | & & \| \\ C_6H_5CH_2N & \!\!-\!\!-\!\! & CH \end{array}$$
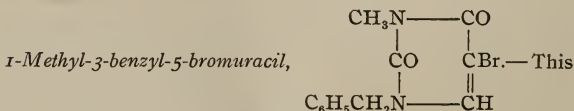
This pyrimidine was prepared in two ways:

[1] Johnson and Heyl: *Loc. cit.*

1. By dissolving 1-methyl-3-benzyluracil in glacial acetic acid and then adding the calculated amount of bromine. They reacted with evolution of heat. The pyrimidine was very soluble in glacial acetic acid but was precipitated by diluting with water.

2. By warming 0.8 gram of 3-benzyl-5-bromuracil in methyl alcohol with 1.9 grams of methyl iodide and 0.1 gram of metallic sodium. The alkylation was very smooth and the solution was neutral in a few minutes. The pyrimidine crystallizes from alcohol in diamond-shaped prisms melting at 123° to a clear oil with no effervescence. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{11}O_2N_2Br$.	Found.
N	9.50	9.8

2-Ethylmercapto-1-benzyl-5-methyl-6-oxypyrimidine,

$C_6H_5CH_2N$——CO

C_2H_5SC CCH_3.—Fifteen grams of 2-ethylmercapto-5-

N——CH

methyl-6-oxypyrimidine and 4.9 grams of finely pulverized potassium hydroxide were dissolved in 75 cc. of absolute alcohol. Eleven and two-tenths grams of benzyl chloride were then added and the solution heated on the steam bath for 6 hours. After filtering from undissolved potassium chloride and evaporation of the alcohol we obtained a crystalline product which was washed with 50 cc. of a 5 per cent solution of sodium hydroxide. Four and four-tenths grams of unaltered pyrimidine deposited when the sodium hydroxide solution was acidified with acetic acid. The crystalline material, insoluble in sodium hydroxide, was then extracted in the usual manner with ether and the insoluble portion saved (see 3-benzyl derivative below). From the ether washings we obtained about 3.0 grams of pyrimidine melting at 65°–66°. The compound is very soluble in acetone, benzene, and ether. It separates from dilute alcohol in stout prisms melting at 70° to a clear oil without effervescence. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{16}ON_2S$.	Found.
N	10.77	10.9

2-Ethylmercapto-3-benzyl-5-methyl-6-oxypyrimidine,

$$\begin{array}{c} \text{N}\underline{}\text{CO} \\ \| \qquad | \\ \text{C}_2\text{H}_5\text{SC} \qquad \text{CCH}_3. \\ | \qquad \| \\ \text{C}_6\text{H}_5\text{CH}_2\text{N}\underline{}\text{CH} \end{array}$$ — The crystalline material, which was
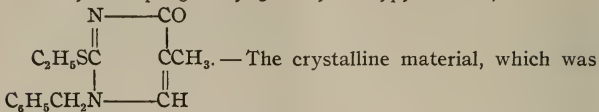
insoluble in ether, in the above experiment represented this pyrimidine and weighed 11.2 grams, corresponding to 68 per cent of the calculated. The pyrimidine is extremely soluble in alcohol and acetone. It was purified for analysis by recrystallization from benzene. It separated in hexagonal plates melting at 121°–122°. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{16}ON_2S$.	Found.
N	10.77	11.1

1-Benzylthymine,

$$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{N}\underline{}\text{CO} \\ | \qquad | \\ \text{CO} \qquad \text{CCH}_3. \\ | \qquad \| \\ \text{NH}\underline{}\text{CH} \end{array}$$ — One and eight-

tenths grams of 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine were digested with concentrated hydrochloric acid until the evolution of ethyl mercaptan ceased. When this solution was evaporated to dryness the benzylthymine was obtained as a crystalline compound. The pyrimidine separated from hot alcohol in clusters of radiating prisms which melted at 204°–205° to a clear oil. The pyrimidine is difficultly soluble in water. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2$.	Found.
N	12.96	13.3

This compound reacted with diazobenzenesulphonic acid, in presence of sodium hydroxide, giving a beautiful, claret red solution.

3-Benzylthymine,

$$\begin{array}{c} \text{NH}\underline{}\text{CO} \\ | \qquad | \\ \text{CO} \qquad \text{CCH}_3. \\ | \qquad \| \\ \text{C}_6\text{H}_5\text{CH}_2\text{N}\underline{}\text{CH} \end{array}$$ — A quantitative
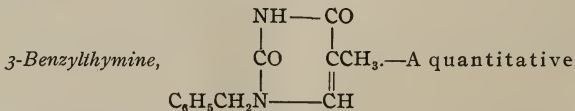
yield of this pyrimidine was obtained when the corresponding

2-mercaptopyrimidine was digested with concentrated hydrochloric acid until the evolution of ethyl mercaptan ceased. The pyrimidine is easily soluble in alcohol, acetone, benzene, and difficultly soluble in ether. It is very soluble in glacial acetic acid and chloroform and difficultly soluble in cold 25 per cent hydrochloric and sulphuric acids. It separates from hot water in diamond-shaped prisms melting at 160° to a clear oil with no effervescence. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2$.	Found.
N	12.96	13.2

This pyrimidine did not react with diazobenzenesulphonic acid to give a red color. The mixture assumed a yellow color which remained permanent for over one hour.

Solubility of 3-Benzylthymine in Water.—One hundred parts of water dissolved at 25°

I.	II.
0.1172 gram.	0.1174 gram.

1-Methyl-3-benzylthymine,

$$CH_3N\!-\!\!-\!\!-\!CO$$
$$|\qquad\quad|$$
$$CO\quad\ CCH_3\text{.— From 3-}$$
$$|\qquad\ \|$$
$$C_6H_5CH_2N\!-\!\!-\!\!-\!CH$$
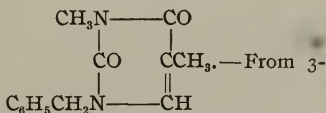
benzylthymine and methyl iodide. It crystallized from water in prismatic crystals melting at 101° to a clear oil. It did not react with diazobenzenesulphonic acid to give a red color. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}O_2N_2$.	Found.
N	12.17	12.07

*3-*p-*Nitrobenzyloxynitrohydrothymine,*

$$NH\!-\!CO$$
$$|\qquad\ |\quad CH_3$$
$$CO\quad\ C\!<$$
$$|\qquad\ |\quad NO_2$$
$$NO_2C_6H_4CH_2N\!-\!\!-\!CHOH$$
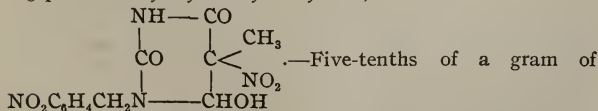
.—Five-tenths of a gram of 3-benzylthymine was dissolved in 10 cc. of cold fuming nitric acid of density 1.5. There was only slight evolution of heat

and the pyrimidine dissolved to a clear, yellow solution. On standing exposed to the atmosphere well-developed prisms separated. They decomposed at 176° with violent effervescence. A nitrogen determination indicated that a nitro group had entered the benzene ring and that nitric acid had added to the double bond in the 4,5 positions of the pyrimidine ring. Analysis (Kjeldahl):

	Calculated for			
	$C_{12}H_{12}O_7N_4$.	$C_{12}H_{13}O_5N_3$.	$C_{12}H_{11}O_4N_3$.	Found.
N	17.28	14.33	16.0	17.11

NEW HAVEN, CONN.,
June, 1908.

CLXII.—RESEARCHES ON HALOGEN AMINO ACIDS: PARAIODPHENYLALANINE.

[FIFTH PAPER.]

BY HENRY L. WHEELER AND SAMUEL H. CLAPP.

Our work on the halogen substitution products of phenylalanine has now been extended so as to include *p*-iodphenylalanine. The starting point for the preparation of this acid was *p*-iodtoluene, melting at 35°–36°. This was converted into *p*-iodbenzyl bromide as described by Jackson.[1] When this reactive halide was heated with the sodium salt of phthalimidomalonic ester, in the manner described by Sörensen[2] in his synthesis of phenylalanine, an almost quantitative reaction took place as follows:

$$IC_6H_4CH_2Br + NaC(CO_2C_2H_5)_2N(CO)_2C_6H_4 =$$
$$IC_6H_4CH_2C(CO_2C_2H_5)_2N(CO)_2C_6H_4 + NaBr.$$
$$I.$$
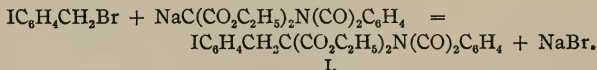
When *p*-iodbenzylphthalimidomalonic ester, I., thus formed, was warmed with alkali and the solution acidified with hydrochloric acid while warm, carbon dioxide was evolved and the phthalamic acid, III., separated. If the solution was acidi-

[1] THIS JOURNAL, **1**, 103 (1879).

[2] Compt. rend. Trav. Lab. Carlsberg, **6**, 6 (1902); Centrabl., **1903**, II., 33; Z. physiol. Chem., **44**, 448 (1905).

fied while cold, a mixture of the two phthalamic acids, II. and III., was obtained.

$$IC_6H_4CH_2C(COOH)_2NHCOC_6H_4COOH,$$
II.

$$IC_6H_4CH_2CH(COOH)NHCOC_6H_4COOH.$$
III.
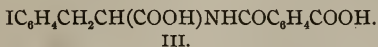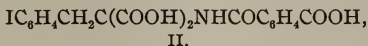
Even a moderate treatment of the phthalamic acids with hot hydrochloric acid was sufficient to effect hydrolysis of the acid amide group, and on evaporating a mixture of phthalic acid and *p*-iodphenylalanine hydrochloride was obtained. Phthalic acid was dissolved and the free *p*-iod-phenylalanine, IV., was obtained by dissolving the mixture in ammonia and then evaporating or precipitating with acetic acid.

$$C_6H_4 \Big\langle {CH_2CH(NH_2)COOH(1) \atop I(4)}$$
IV.
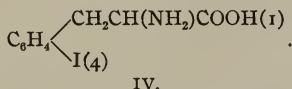
p-Iodphenylalanine and the intermediate compounds in the present synthesis immediately liberate iodine when treated with concentrated sulphuric acid. Iodine vapors fill the flask in the Kjeldahl analyses. The substances are far more stable towards concentrated hydrochloric acid. No iodine was removed by this acid when the solutions were digested on the steam bath for a few hours. Iodine was not removed in the above synthesis if the treatment with alkali was not too energetic. If the alcoholic solution of phthalimidomalonic ester was warmed too long with alkali, iodine could then be detected by treating the solution with dilute sulphuric acid and potassium nitrite and then shaking with chloroform.

It is noteworthy that *p*-iodphenylalanine or its silver salt can be boiled with an aqueous solution of silver nitrate and nitric acid without separating silver iodide. On the other hand iodgorgoic acid or diiodtyrosine readily gives up all of the iodine as silver iodide by this treatment.[1] The

[1] Wheeler and Jamieson: This Journal, **33**, 365 (1905).

separation of silver iodide in the case of diiodtyrosine is quite characteristic. The clear solution on warming suddenly becomes turbid *just as the boiling point is reached* and the yellow solid causing the turbidity soon after separates as a heavy precipitate with the characteristic appearance of silver iodide.

Since diiodtyrosine contains 58.6 per cent of iodine this reaction serves as a delicate test for the acid.

It is now interesting to note that when sponges are boiled with barium hydroxide a solution containing an iodamino acid is obtained which separates silver iodide in precisely the same manner as described above when heated with a solution of silver nitrate and nitric acid.

EXPERIMENTAL PART.

p-Iodbenzyl Bromide, $C_6H_4{<}^{CH_2Br(1)}_{I(4)}$.—*p*-Iodtoluene, from Kahlbaum, was distilled at about 25 mm. pressure. It boiled at 113° and solidified to a light yellowish, crystalline mass melting at 35°–36°. This was converted into *p*-iodbenzyl bromide[1] as follows: Twenty grams of bromine were added in small drops to 25.8 grams of *p*-iodtoluene heated in an oil bath. The temperature of the bath at first was 180°, then it was kept at 170°. About 15 minutes was taken to add the bromine. On cooling, the contents of the flask solidified to a dark colored, crystalline mass. This was treated with small quantities of cold alcohol, which removed the color, and on filtering and washing thoroughly with cold alcohol 17.7 grams of *p*-iodbenzyl bromide, melting at 75°–78°, were obtained. From the alcoholic washings, on evaporating at ordinary temperature, 1.6 grams more of the bromide were obtained. This made the yield 54.8 per cent of the calculated. The remaining material was a dark colored oil which did not solidify after standing a long time in the open air.

In another experiment 55.3 grams of *p*-iodtoluene and 41.0 grams of bromine at 140°–145°, taking about one-half hour

[1] Jackson: *Loc. cit.* See also Jackson and Mabery: THIS JOURNAL, **2**, 250 (1880).

to add the bromine, gave 34.7 grams of *p*-iodbenzyl bromide. This yield is 46 per cent of the calculated.

p-Iodbenzylphthalimidomalonic Ester,

$IC_6H_4CH_2C(CO_2C_2H_5)_2N(CO)_2C_6H_4$.—Seventeen grams of *p*-iod-benzyl bromide were added to the dry sodium salt of phthal-imidomalonic ester, prepared according to Sörensen's directions from 17.5 grams of phthalimidomalonic ester and 1.3 grams of sodium. The mixture was heated for several hours in an oil bath at 130°–140°. It reacted slowly, the yellow color became lighter, and the mass liquefied. The temperature of the bath was then maintained at 150°–160° until the original yellow color disappeared. The flask was then cooled and the contents extracted with 100 cc. of hot water. The undissolved material was crystallized from alcohol. Beautiful, flat, colorless prisms or six-sided plates separated. They melted at 112° to a clear oil. The yield was 24.5 grams or 85.8 per cent of the calculated.

  I. 0.1251 gram substance required 2.5 cc. 0.1 N HCl.
 II. 0.3215 gram substance required 6.1 cc. 0.1 N HCl.
III. 0.2024 gram substance gave 0.0911 gram AgI.
 IV. 0.1290 gram substance gave 0.0594 gram AgI.

	Calculated for $C_{22}H_{20}O_6NI$.	I.	II.	Found. III.	IV.
N	2.68	2.79	2.65	...	...
I	24.38	...	...	24.32	24.87

p-Iodbenzylphthalimidomalonic ester is insoluble in water but readily soluble in hot alcohol. Concentrated sulphuric acid immediately liberates iodine. Toward hydrochloric acid the ester is far more stable. Two grams of the ester were dissolved in 100 cc. of 95 per cent alcohol and 25 cc. of concentrated hydrochloric acid were added. The solution was boiled under a return condenser for several hours. It was then evaporated to dryness and the oily residue was crystallized from alcohol. Six-sided plates, which melted at 112° and therefore were unaltered material, separated. There was no evidence of iodine being displaced.

When this ester is warmed with dilute alkali or barium

hydroxide it is readily saponified and it was found that the solutions could be boiled for a moderate length of time without giving a test for iodine when treated with sodium nitrite, acidified with sulphuric acid, and shaken with chloroform.

Sixteen grams of the ester, dissolved in a small amount of boiling alcohol, and 6.9 grams of potassium hydroxide in 400 cc. of water gave no test for iodine as above when warmed on the steam bath for 10 minutes, although the ester was saponified.

When the same quantities were warmed a half hour a faint test for iodine was obtained.

p-Iodbenzylaceticphthalamic Acid,
$IC_6H_4CH_2CH(COOH)NHCOC_6H_4COOH$.—Seven and one-half grams of the above ester were dissolved in alcohol and 5 grams of potassium hydroxide in a little water were added to the hot solution. The solution was warmed for an hour on the steam bath, the alcohol evaporated, and the residue taken up in water and acidified with hydrochloric acid. The precipitate thus obtained, melting at 178°, weighed 6.3 grams, which corresponds with the calculated. The solution, however, gave a test for iodine.

When the material is precipitated from hot alkaline solutions by means of hydrochloric acid it separates in the form of fine looking needles melting at 178°–179°, otherwise it separates in a doughy or stringy condition.

In one experiment ten grams of *p*-iodbenzylphthalimido-malonic ester were dissolved in 50 cc. of 95 per cent alcohol and to the hot solution 4.0 grams of sodium hydroxide in 30 cc. of water were added. Three grams sodium hydroxide is the calculated amount for 4 molecules. The solution remained clear immediately after the addition of the alkali but in a few minutes a heavy mass of crystals of the sodium salt separated. It is evident from this that the saponification takes place with alkali with ease.

The flask was left on the steam bath a few minutes after the sodium salt had separated, whereupon the solution suddenly bumped so violently that almost half the material was lost. The alkaline solution gave no color test for iodine with

sodium nitrite and sulphuric acid. When precipitated with hydrochloric acid, after evaporating the alcohol, and warmed, the doughy mass first obtained was seen to be full of bubbles (carbon dioxide). Some of this precipitate dissolved and then in a few minutes needles separated from the warm solution and the undissolved material changed to a granular powder. Both the needles and the powder melted with effervescence at 179°. This material is practically insoluble in water, but very soluble in alcohol.

Analyses of the needles:

I. 0.2625 gram substance required 6.1 cc. 0.1 N HCl.
II. 0.2200 gram substance required 5.0 cc. 0.1 N HCl.

	Calculated for $C_{17}H_{14}O_5NI$.	Found. I.	II.
N	3.19	3.25	3.18

The saponification with alkali does not usually stop precisely at this phthalamic acid, a portion of the material being further hydrolyzed to *p*-iodphenylalanine. The compounds can be separated by means of alcohol.
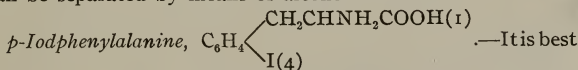
p-Iodphenylalanine, $C_6H_4\begin{smallmatrix}CH_2CHNH_2COOH(1)\\I(4)\end{smallmatrix}$.—It is best to saponify the *p*-iodbenzylphthalimidomalonic ester with potassium hydroxide. The solution is less liable to bump. The precipitate produced, after evaporation of the alcohol, by the addition of hydrochloric acid was digested with 20 per cent hydrochloric acid for about two hours on the steam bath. No iodine appeared to be liberated in this treatment. On concentrating to a small volume and adding concentrated hydrochloric acid the amino acid can be precipitated as the hydrochloride. The precipitate, however, contains phthalic acid. It was found best to evaporate to dryness, then treat the residue with a little water, and evaporate again to dryness. The residue was dissolved in ammonia and the *p*-iodphenylalanine either precipitated by acetic acid (Analysis III. The yield was almost quantitative), or the ammonia solution was evaporated on the steam bath. For example,

1.5 grams of the acid were dissolved in strong ammonia and the ammonia evaporated. Clusters of thin scales, which weighed 1.1 grams, separated when the solution had no odor of ammonia (Analysis II.). The filtrate deposited another crop of plates on further evaporation, and it gave a test for iodine with potassium nitrite and sulphuric acid.

If the hydrochloric acid solution is evaporated to dryness, taken up in water, the operation repeated, and the residue then boiled with water and alcohol, the hydrochloric acid salt dissociates and free *p*-iodphenylalanine remains undissolved. (Analysis I.).

    I. 0.2434 gram substance required 8.4 cc. 0.1 N HCl.

    II. 0.2460 gram substance required 8.7 cc. 0.1 N HCl.

    III. 0.1394 gram substance gave 0.1119 gram AgI (Carius).

	Calculated for $C_9H_{10}O_2NI$.	I.	Found. II.	III.
N	4.81	4.83	4.95	...
I	43.64	...	...	43.38

p-Iodphenylalanine is very slightly soluble in water even at 100°. It is also very sparingly soluble in alcohol. It is readily dissolved by hot acetic acid and this is the best solvent from which to crystallize the substance. It forms thin scales with an irregular outline and the resemblance to phenylalanine is very striking. It melts to an oil with vigorous effervescence at 270°. The melting point may vary a few degrees according to the rate of heating.

A solution of the acid in 20 per cent sulphuric acid is partially precipitated by a strong solution of phosphotungstic acid in 5 per cent sulphuric acid. The precipitate dissolves on warming and does not form if acetic acid is present. The ammonia solution of the acid gave no precipitate with barium chloride. About 0.2 gram of the acid was dissolved in 100 cc. of a solution of barium hydroxide, saturated at ordinary temperature, and this solution was allowed to digest on the steam bath for about a week. It was then filtered from some barium carbonate and acidified with nitric acid. On adding silver nitrate no silver iodide was precipitated.

Action of Sodium Hydroxide.—One-tenth gram of *p*-iod-phenylalanine was boiled for a few minutes in an open flask with about 5 cc. of 33 per cent sodium hydroxide. On cooling, a crystalline sodium salt separated, difficultly soluble in sodium hydroxide and very readily soluble in water. Under these conditions no iodine could be detected in this solution with nitrous acid.

In a second experiment about 0.2 gram of *p*-iodphenyl-alanine was warmed on the water bath with 20 cc. of 33 per cent sodium hydroxide for five and a half hours. The solution then gave a pronounced test for iodine with nitrous acid and a very weak Millon's reaction. The solution was warmed for 5 hours longer on the water bath, made weakly acid with hydrochloric acid, and then weakly alkaline with ammonia. After filtering from inorganic material the solution was concentrated. About 0.1 gram of substance, practically insoluble in boiling water, which contained iodine and was therefore unaltered *p*-iodphenylalanine, separated out.

The hydrochloride, $IC_6H_4CH_2CH(NH_2HCl)COOH$, was prepared by dissolving *p*-iodphenylalanine in hot dilute hydrochloric acid and then adding concentrated hydrochloric acid. It separated in clusters of very thin, flat, colorless plates with irregular outlines. It is very insoluble in strong hydrochloric acid and it is dissociated by boiling water. It was dried over sulphuric acid and potassium hydroxide.

0.0985 gram substance gave 0.0424 gram AgCl.

	Calculated for $C_9H_{10}O_2NI.HCl$.	Found.
Cl	10.84	10.64

This salt decomposed at about 248° when not too slowly heated.

The silver salt was prepared by adding an aqueous solution of silver nitrate to a neutral solution of the acid in ammonia, or to a solution of the acid in 0.1 N potassium hydroxide. It forms a white, nongelatinous precipitate which is readily soluble in ammonia or dilute nitric acid. It differs decidedly from the silver salt of diiodtyrosine inasmuch as the nitric

acid solution can be boiled for some time without the separation of silver iodide.

The Copper Salt, $(IC_6H_4CH_2CH(NH_2)COO)_2Cu$.—*p*-Iodphenylalanine dissolved in the calculated quantity of 0.1 N sodium hydroxide gave a light blue, gelatinous precipitate with copper sulphate. When boiled with water it became more granular but it showed no characteristic crystalline form. When dried in the air it formed a light blue powder. It was almost insoluble in boiling water and alcohol and it did not lose weight at 85°–90°.

0.1693 gram substance gave 0.0214 gram CuO.

	Calculated for $C_{18}H_{18}O_4N_2I_2Cu$.	Found.
Cu	9.88	10.10

The phenylisocyanate derivative was prepared by dissolving *p*-iodphenylalanine in the calculated quantity of 0.1 N sodium hydroxide and then adding a slight excess of phenyl isocyanate. Some heat was evolved and a crystalline mass of diphenylurea and the sodium salt of the hydantoic acid separated. Water was added and the solution, on filtering and acidifying with hydrochloric acid, deposited the hydantoic acid as an oil which solidified to a crystalline mass. The substance is insoluble in water and petroleum ether. It is readily soluble in alcohol and very soluble in ether. It crystallizes from alcohol in aggregates of flat prisms or plates, best on adding a little water. It melts at 178°–179° with brisk effervescence.

0.1656 gram substance required 8.0 cc. 0.1 N HCl.

	Calculated for		Found.
	$C_{16}H_{15}O_2N_2I$ (hydantoin).	$C_{16}H_{15}O_3N_2I$.	
N	7.14	6.83	6.76

The *hydantoin* was prepared by boiling the above phenyl isocyanate derivative with 20 per cent hydrochloric acid for 3 hours. The hydrochloric acid was then evaporated and the material was crystallized from alcohol. It was found to be much less soluble in alcohol than the hydantoic acid and

it formed large, flat, rhombohedral crystals. It melted to a clear oil without effervescence at 195°–196°.

0.1069 gram of substance required 5.7 cc. 0.1 N HCl.

	Calculated for $C_{16}H_{18}O_2N_2I$.	Found.
N	7.14	7.46

p-Iodphenylalanine Ethyl Ester, $IC_6H_4CH_2CH(NH_2)COOC_2H_5$. —Three and seven-tenths grams of *p*-iodphenylalanine were suspended in 200 cc. of absolute alcohol and a rapid stream of dry hydrogen chloride was passed through the solution without cooling; the precipitate went rapidly into solution. The solution was then evaporated to dryness under diminished pressure. The crystalline residue was suspended in 200 cc. of absolute alcohol and the operation repeated. The residue was dissolved in ice water, ether was added, the solution containing the hydrochloride was neutralized with 33 per cent sodium hydroxide, and the free ester at once removed in the ether. The ether solution was shaken 15 minutes with anhydrous potassium carbonate, and dried for two days over anhydrous sodium sulphate. The ether was then evaporated on the water bath and a thick oil was obtained, from which, when cooled, a small amount of gelatinous solid separated. This went into solution again on warming. The whole was distilled at about 25 mm. pressure, whereupon the oil practically all boiled at 223°–226°. The weight of distilled ester was 2 grams or 50 per cent of the calculated. During the distillation no evidence of decomposition was observed. A very small amount of crystalline residue remained in the distilling bulb.

The *p*-iodphenylalanine ethyl ester formed a thick, colorless oil difficultly soluble in water, which was converted into the picrate for analysis.

The Picrate, $IC_6H_4CH_2CH(NH_2)COOC_2H_5.C_6H_3O_7N_3$.—The distilled oil was dissolved in alcohol and an aqueous solution of picric acid in excess was added. The yellow precipitate was recrystallized from alcohol. It then formed flat plates

or tables which melted to a clear red oil, without conspicuous effervescence, at 200°–203°.

0.1250 gram substance required 9.3 cc. 0.1 N HCl.

	Calculated for $C_{11}H_{14}O_2NI.C_6H_3O_7N_3$.	Found.
N	10.22	10.42

New Haven, Conn.,
June, 1908.

A STUDY OF THE REFRACTIVE INDICES OF SOME SOLUTIONS.

By Frederick H. Getman and F. B. Wilson.

In their recent work on hydration in solution, Jones and Getman[1] measured the refractive indices of the solutions studied in order to determine whether there was any minimum in the refractivity-concentration curves similar to that found in the freezing point-concentration diagrams. In every case the refractive index was found to be a linear function of the concentration. From this the authors concluded that the measurement of the refractive index of a solution does not enable one to determine whether hydration has taken place or not. If combination between solute and solvent does occur, or if owing to the attraction of the solute some of the solvent is removed from the rôle of purely solvent action, then we should expect some change in the refractive power of the solution.

With a view to further testing this point the present investigation was undertaken.

Instead of following the change in refractive index with change in concentration of the solution, we have compared specific refractions with corresponding concentrations. The relation of specific refraction, R, to refractive index is given by the empirical formula of Gladstone and Dale,[2]

$$\frac{n-1}{d} = R,$$

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[1] Z. physik. Chem., **46**, 244. Phys. Rev., **18**, 146. This Journal, **31**, 303. Z. physik. Chem., **49**, 407. Pub. No. 60, Carnegie Institution.
[2] Phil. Trans., **1858**, 887.

where n is the refractive index and d is the density of the solution. Other formulae for specific refraction have been proposed, notably those of Newton, Lorenz-Lorentz, and Edwards. The Gladstone and Dale formula was selected in preference to any of the others because of its being quite independent of slight changes in temperature, as has been pointed out by Landolt.[1]

The apparatus employed for the measurement of the refractive indices of the solutions was a Pulfrich refractometer made by Wolz. This form of instrument, not being furnished with any temperature regulating device, has the disadvantage that both prism and solution are subject to the same thermal variation as the air of the room. The temperature of the room remained very nearly constant throughout the work, the greatest variation being five degrees. An attempt was made to bring all of the measurements to one temperature by heating and cooling the solutions and thus working out a table of temperature coefficients for several concentrations of each solution. This proved to be impracticable since we possessed no means of determining when thermal equilibrium was finally established between prism and solution. By using the Gladstone and Dale formula, however, it is certain that no appreciable error can be traced to temperature variations. All measurements of refractive indices were made for the D line, a Bunsen flame fed with sodium chloride being the source of light.

The densities of the solutions were taken from the tables of Landolt and Börnstein and the Smithsonian Physical Tables.

All solutions were made up on the percentage basis. Some of the data recorded in this paper have been calculated from the measurements of refractive indices made by other workers. Where such material has been drawn upon, suitable acknowledgment will be made in the proper place.

If the specific refraction of a solution of definite percentage concentration is known and the specific refraction of the solvent is also determined, the specific refraction of the solute

[1] Pogg. Ann., **123**, 595.

may be easily calculated. In Fig. I., let O be the origin of a system of rectangular coördinates, in which abscissae denote percentage concentrations and ordinates specific refractions. Let A represent the pure solvent of specific refraction R, let B denote the solution of concentration p and specific refraction R_1, and let C be the pure solute whose specific refraction R_2 is sought.
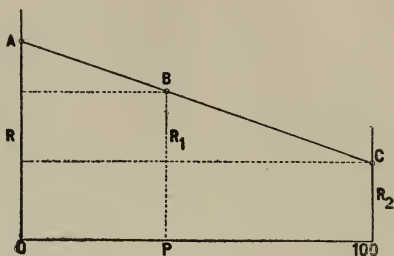
Fig. I.

From the diagram it is evident that

$$\frac{R - R_1}{p} = \frac{R - R_2}{100},$$

or

$$R_2 = R - \frac{100(R - R_1)}{p} \qquad (1).$$

Substituting $(n - 1)/d$, $(n_1 - 1)/d_1$, and $(n_2 - 1)/d_2$ for R, R_1, and R_2 respectively, in (1), we get

$$\frac{n_2 - 1}{d_2} = \frac{n_1 - 1}{d_1} \cdot \frac{100}{p} - \frac{n - 1}{d} \cdot \frac{100 - p}{p} \qquad (2).$$

Equation (2) is identical with that used by Gladstone and Dale[1] for the calculation of the specific refraction of a solid from its solution.

These authors found close agreement between the specific refraction determined from the solution and that determined

[1] Phil. Trans., 1858, 887.

directly from the pure solute. Subsequent work by other investigators, notably Bedson and Williams,[1] Kanonnikow,[2] Nasini,[3] Damien,[4] LeBlanc,[5] and F. Schütt,[6] has failed to confirm the original statements of Gladstone and Dale. In some cases there is marked discrepancy between the values of specific refractivity as calculated from a solution and that determined directly from the solute. This difference appears to be greater when the solute is a salt than when it is a non-electrolyte. In explanation of this Ostwald says: "die Zustandsänderung, welche ein Salz beim Auflösen im Wasser erfährt, sehr viel tiefer gehender Natur ist, als die, welche indifferente Stoffe erleiden."[7]

Then, too, many salts form anisotropic crystals whose refractive constants are different in different directions. This may partially account for the lack of agreement between the specific refraction as calculated from the solution and as determined from the pure salt.

The specific refraction of a salt may also be calculated from the refractive equivalents of its constituent elements. Landolt[8] has shown that the sum of the refractive equivalents of the elements which enter into a compound, divided by its molecular weight, gives the specific refraction of the compound.

Here also there is not perfect agreement between the specific refraction calculated from the refraction equivalents and that found by direct measurements of the refractive index and density of the solid substance.

The differences between the values of the specific refractions as calculated and observed for fifteen of the substances studied in this paper are given in Table I.:

[1] Ber. d. chem. Ges., **14**, 2549.
[2] J. prakt. Chem. [2], **31**, 321.
[3] Accad. dei Lincei, 8, 1884.
[4] Ann. de l'Ecole Norm. Sup. [2], 10.
[5] Z. physik. Chem., **4**, 559.
[6] *Ibid.*, **5**, 349.
[7] "Lehrb. allg. Chem.," I., 429.
[8] Wied. Ann., **123**, 611.

Table I.

Solute.	R (calc.).	R (obs.).	Solute.	R (calc.).	R (obs.).
NaCl	0.2649	0.2426	$CuSO_4.5H_2O$	0.2632	0.2318
$NaNO_3$	0.2211	0.2593	CH_3COOH	0.3567	0.3525
KCl	0.2486	0.2459	$n\text{-}C_3H_7COOH$	0.4159	0.4122
KBr	0.2079	0.2029	CH_3OH	0.4062	0.4122
KI	0.2144	0.2171	C_2H_5OH	0.4478	0.4506
KNO_3	0.2131	0.2397	$C_3H_5(OH)_3$	0.3673	0.3738
K_2CrO_4	0.2722	0.2666	$C_{12}H_{22}O_{11}$	0.3491	0.3585
$CaCl_2.6H_2O$	0.2913	0.2521			

Because of this lack of agreement between the observed and calculated values of R and because the indices of refraction of several of the salts studied have not been measured, it was decided to use only the values of specific refractions calculated from refractive equivalents. Further, when a salt has water of crystallization the specific refraction has been uniformly calculated for the anhydrous salt.

Before measuring the refractive indices of any solutions the refractive index of pure water was determined at several temperatures and the corresponding specific refraction calculated by means of the Gladstone and Dale formula.

Table II. shows the values of the index for water at different temperatures and also gives the specific refraction R, as calculated. The temperature coefficient of refraction is also tabulated, but as was pointed out above, the form of refractometer used does not admit of sufficiently accurate control of the temperature to render these coefficients trustworthy. The table also emphasizes what was said as to the Gladstone and Dale formula being quite independent of temperature changes.

Table II.—Water.

t.	d.	n.	dn/dt.	$(n-1)/d = R$.
15	0.99916	1.33379	.....	0.3341
22.6	0.99769	1.33309	0.000092	0.3337
30	0.99577	1.33239	0.000094	0.3338
35	0.99418	1.33193	0.000092	0.3338
40	0.99235	1.33139	0.000108	0.3338

Mean, 0.3338

The salts used in this investigation were obtained from Kahlbaum. The solutions were made up on the percentage basis with pure distilled water, the most concentrated solution for each salt being almost saturated. Several concentrations of each solute were prepared and the refractive indices measured, and from the tables of densities the specific refractions were calculated. By means of equation (2) the specific refraction of the solute was calculated from the specific refraction of each solution, the value of the specific refraction of water being taken as 0.3338.

The measurements and the calculated data are recorded in the following tables. In these tables the notation is as follows: p = percentage concentration, d = density, n = index of refraction, R_1 and R_2 = specific refraction of solution and solute, respectively.

Table III.—Sodium Chloride-Water. $(t = 18°.1)$.[1]

p.	d.	n.	R_1.	R_2.
1	1.0072	1.33525	0.3328	0.2239
2	1.0145	1.33701	0.3321	0.2449
5	1.0362	1.34225	0.3303	0.2619
10	1.0733	1.35103	0.3271	0.2659
15	1.1114	1.35994	0.3238	0.2672
20	1.1510	1.36897	0.3205	0.2669
25	1.1922	1.37824	0.3172	0.2671

Mean, 0.2568

Table IV.—Sodium Iodide-Water. $(t = 18°)$.[2]

p.	d.	n.	R_1.	R_2.
10	1.082	1.34445	0.3183	0.1779
20	1.179	1.36760	0.3118	0.2234
30	1.294	1.39075	0.3019	0.2283
40	1.432	1.42890	0.2925	0.2304

Table V.—Sodium Nitrate-Water. $(t = 22°.8)$.

p.	d.	n.	R_1.	R_2.
16.9	1.1178	1.35183	0.3147	0.2206
44.4	1.3580	1.38538	0.2838	0.2187

Mean, 0.2197

[1] Schütt: Z. physik. Chem., **9**, 351.
[2] Bender: Wied. Ann., **39**, 90.

Table VI.—Sodium Carbonate-Water. $(t = 20°.5)$.

p.	d.	n.	R_1.	R_2.
1.42	1.0151	1.33624	0.3312	0.1438
2.80	1.0291	1.33944	0.3298	0.1793
6.73	1.0715	1.34771	0.3245	0.1983
12.7	1.1379	1.34990	0.3154	0.1878

Table VII.—Potassium Chloride-Water. $(t = 20°)$.

p.	d.	n.	R_1.	R_2.
5	1.03250	1.33975	0.3291	0.2369
10	1.06580	1.34650	0.3250	0.2449
15	1.10036	1.35368	0.3214	0.2502
20	1.13608	1.36127	0.3171	0.2499
24	1.16568	1.36960	0.3171	0.2638

Mean, 0.2491

Table VIII.—Potassium Bromide-Water. $(t = 20°)$.

p.	d.	n.	R_1.	R_2.
5	1.037	1.33900	0.3269	0.1939
10	1.070	1.34515	0.3226	0.2206
15	1.116	1.35178	0.3152	0.2086
20	1.159	1.35875	0.3096	0.2124
25	1.207	1.36628	0.3034	0.2119
30	1.256	1.37418	0.2979	0.2051

Mean, 0.2087

Table IX.—Potassium Iodide-Water. $(t = 20°)$.

p.	d.	n.	R_1.	R_2.
5	1.038	1.34008	0.3276	0.2079
10	1.078	1.34665	0.3216	0.2106
15	1.120	1.35460	0.3166	0.2180
20	1.166	1.36250	0.3109	0.2189
25	1.218	1.37145	0.3049	0.2179
30	1.271	1.38115	0.2998	0.2114
35	1.331	1.39125	0.2939	0.2119
40	1.396	1.40220	0.2881	0.2194
50	1.546	1.42835	0.2771	0.2202

Mean, 0.2151

Table X.—Potassium Nitrate-Water. $(t = 21°)$.

p.	d.	n.	R_1.	R_2.
1	1.0065	1.33426	0.3221	0.1539
2	1.0131	1.33521	0.3308	0.1789
3	1.0197	1.33600	0.3295	0.1874
4	1.0264	1.33690	0.3282	0.1914
5	1.0300	1.33773	0.3278	0.2119
10	1.0621	1.34240	0.3224	0.2187
15	1.0956	1.34735	0.3170	0.2207
20	1.1316	1.35263	0.3116	0.2224

Mean, 0.1923

Table XI.—Potassium Chlorate-Water. $(t = 20°)$.

p.	d.	n.	R_1.	R_2.
1	1.007	1.33426	0.3319	0.1339
1.5	1.010	1.33465	0.3313	0.1591
2	1.014	1.33505	0.3304	0.1589
4	1.026	1.33665	0.3281	0.1889
6	1.039	1.33833	0.3256	0.1953

Mean, 0.1672

Table XII.—Potassium Chromate-Water. $(t = 20°)$.

p.	d.	n.	R_1.	R_2.
3	1.0243	1.33973	0.3316	0.2573
4	1.0325	1.34187	0.3309	0.2489
5	1.0408	1.34401	0.3305	0.2659
10	1.0837	1.35525	0.3278	0.2729
15	1.1287	1.36715	0.3253	0.2763
20	1.1765	1.37940	0.3224	0.2754
25	1.2274	1.39233	0.3196	0.2767
30	1.2808	1.40525	0.3164	0.2661
35	1.3386	1.41985	0.3136	0.2671

Mean, 0.2674

Table XIII.—Lithium Chloride-Water. $(t = 20°)$.[1]

p.	d.	n.	R_1.	R_2.
4.2	1.0243	1.34243	0.3343	0.3444
8.76	1.0508	1.35154	0.3345	0.3407
20.3	1.1191	1.37595	0.3359	0.3437
33	1.2040	1.40460	0.3360	0.3402

[1] Walter: Wied. Ann., **42**, 511.

Table XIV.—Calcium Chloride-Water. $(t = 25°)$.[1]

p.	d.	n.	R_1.	R_2.
33	1.143	1.37152	0.3250	0.3072
48	1.215	1.39411	0.3243	0.3137
83	1.398	1.44000	0.3140	0.3100

Table XV.—Cupric Chloride-Water. $(t = 15°)$.[2]

p.	d.	n.	R_1.	R_2.
5.17	1.0462	1.34790	0.3325	0.3068
38.2	1.4983	1.45490	0.3036	0.2545

Table XVI.—Copper Sulphate-Water. $(t = 20°)$.[3]

p.	d.	n.	R_1.	R_2.
5.58	1.0357	1.34381	0.3319	0.2881
15.05	1.0995	1.36267	0.3298	0.3065
16.79	1.1120	1.36619	0.3293	0.3068

Table XVII.—Zinc Chloride-Water. $(t = 26°.5)$.[4]

p.	d.	n.	R_1.	R_2.
23	1.2090	1.37515	0.0103	0.2324
36	1.3590	1.40222	0.2959	0.2305

Mean, 0.2315

Table XVIII.—Cadmium Chloride-Water. $(t = 15°)$.[5]

p.	d.	n.	R_1.	R_2.
14.8	1.140	0.35880	0.3174	0.2014
21.4	1.212	1.37160	0.3066	0.2056
30	1.321	1.38980	0.2951	0.2058
41.5	1.500	1.41978	0.2798	0.2040
57.5	1.831	1.47348	0.2585	0.2057

[1] v. d. Willigen: Arch. Mus. Teyler, **2**, 209.
[2] Walter: *Loc. cit.*
[3] LeBlanc: Z. physik. Chem., **4**, 305.
[4] v. d. Willigen: *Loc. cit.*
[5] de Muynck: Wied. Ann., **53**, 561.

Table XIX.—*Cadmium Iodide-Water.* $(t = 15°)$.[1]

p.	d.	n.	R_1.	R_2.
3.3	1.029	1.33883	0.3292	0.1929
9.6	1.084	1.34846	0.3214	0.2039
13.2	1.111	1.35440	0.3189	0.2199
18.7	1.181	1.36405	0.3082	0.1977
24.2	1.246	1.37483	0.3008	0.1982
31.1	1.336	1.39033	0.2921	0.2001
35.5	1.405	1.40128	0.2856	0.1986
40	1.476	1.41379	0.2803	0.1999

Mean, 0.2014

Table XX.—*Aluminium Chloride-Water.* $(t = 18°)$.

p.	d.	n.	R_1.	R_2.
5	1.0360	1.34625	0.3342	0.3399
10	1.0733	1.35963	0.3351	0.3459
15	1.1124	1.37450	0.3367	0.3524
20	1.1537	1.39063	0.3386	0.3574
25	1.1967	1.40519	0.3389	0.3539
30	1.2421	1.42444	0.3417	0.3596

Table XXI.—*Hydrochloric Acid-Water.* $(t = 20°.8)$.[2]

p.	d.	n.	R_1.	R_2.
34.4	1.1660	1.41109	0.3526	0.3881

Table XXII.—*Nitric Acid-Water.* $(t = 20°)$.[3]

p.	d.	n.	R_1.	R_2.
14.1	1.079	1.35168	0.3259	0.2771
28.7	1.172	1.37235	0.3177	0.2788
40.5	1.250	1.38281	0.3062	0.2647
69.2	1.411	1.40390	0.2862	0.2671

Table XXIII.—*Sulphuric Acid-Water.* $(t = 18°.3)$.[4]

p.	d.	n.	R_1.	R_2.
4.46	1.0298	1.33862	0.3294	0.2439
30.1	1.2270	1.37009	0.3031	0.2323
71.8	1.6340	1.42466	0.2602	0.2307
89.0	1.8190	1.43669	0.2411	0.2270

[1] De Muynck: *Loc. cit.*
[2] v. d. Willigen: *Loc. cit.*
[3] LeBlanc: *Loc. cit.*
[4] v. d. Willigen: *Loc. cit.*

Table XXIV.—Acetic Acid-Water. ($t = 19°$).[1]

p.	d.	n.	R_1.	R_2.
10.5	1.0143	1.33933	0.3345	0.3446
20.9	1.0278	1.34653	0.3371	0.3502
31.1	1.0403	1.35323	0.3395	0.3518
41.3	1.0508	1.35903	0.3417	0.3526
51.3	1.0589	1.36433	0.3440	0.3531
61.3	1.0653	1.36878	0.3461	0.3534
71.1	1.0696	1.37289	0.3486	0.3545
80.8	1.0707	1.37558	0.3508	0.3542
90.5	1.0675	1.37605	0.3522	0.3538
97.7	1.0560	1.37445	0.3546	0.3549

Mean, 0.3525

Table XXV.—Butyric Acid-Water. ($t = 20°$).[2]

p.	d.	n.	R_1.	R_2.
94	0.9663	1.40211	0.4160	0.4209
96	0.9625	1.39946	0.4150	0.4182
98	0.9587	1.39949	0.4167	0.4184

Table XXVI.—Methyl Alcohol-Water. ($t = 20°$).

p.	d.	n.	R_1.	R_2.
7.72	0.98456	1.33505	0.3403	0.4164
15.60	0.97301	1.33727	0.3466	0.4182
37.7	0.94106	1.34147	0.3607	0.4063
40.94	0.93461	1.34229	0.3662	0.4127
41.8	0.93187	1.34227	0.3672	0.4138
56.4	0.90302	1.34221	0.3789	0.4159
65.3	0.88312	1.34106	0.3862	0.4124
72.9	0.86475	1.33903	0.3920	0.4152
86.81	0.83127	1.33348	0.4011	0.4112
94.34	0.81112	1.33123	0.4083	0.4127
100	0.79500	1.32887	....	0.4136

Mean, 0.4123

[1] Landolt: Pogg. Ann., **117**, 353.
[2] Verschaffelt: Bull. Acad. Brux., **27**, 77.

Table XXVII.—*Ethyl Alcohol-Water.* $(t = 25°)$.[1]

p.	d.	n.	R_1.	R_2.
38.8	0.93189	1.35556	0.3815	0.4577
70	0.86853	1.36304	0.4181	0.4545
75	0.85150	1.36324	0.4266	0.4573
79.3	0.84097	1.36332	0.4320	0.4576
80	0.83925	1.35331	0.4209	0.4428
85	0.82674	1.35297	0.4269	0.4437
90	0.81359	1.35239	0.4331	0.4397
95	0.79992	0.35125	0.4391	0.4437
96	0.79700	1.36094	0.4528	0.4576
97	0.79405	1936061	0.4541	0.4577
98	0.79110	1.36024	0.4554	0.4578
99	0.78815	1.35984	0.4565	0.4577
100	0.78510	1.35941		0.4578

Mean, 0.4577

Table XXVIII.—*Glycerol-Water.* $(t = 17°.5)$.[2]

p.	d.	n.	R_1.	R_2.
50	1.1251	1.3973	0.3531	0.3723
60	1.1526	1.4121	0.3567	0.3727
70	1.1800	1.4270	0.3618	0.3730
80	1.2027	1.4421	0.3662	0.3643
90	1.2342	1.4573	0.3705	0.3742
100	1.2600	1.4727		0.3723

Mean, 0.3713

Table XXIX.—*Cane Sugar-Water.* $(t = 17°.5)$.

p.	d.	n.	R_1.	R_2.
5	1.0200	1.34050	0.3338	0.3319
10	1.0404	1.34750	0.3340	0.3349
15	1.0614	1.35570	0.3351	0.3420
20	1.0832	1.36378	0.3358	0.3434
25	1.1059	1.37213	0.3356	0.3407
30	1.1295	1.38086	0.3372	0.3348

Mean, 0.3379

[1] Andrews: J. Am. Chem. Soc., **30**, 353.
[2] Strohmer: Organ östr. Vereins Rübenzucker-Industrie, **21**, 1883.

The data recorded in the foregoing tables are plotted in Figs. II., III., and IV., the abscissae denoting percentage concentration and the ordinates specific refraction. An inspection of the diagrams shows that the curves may be divided into two classes: (1) those in which the experimentally determined specific refractions lie on the straight line joining the
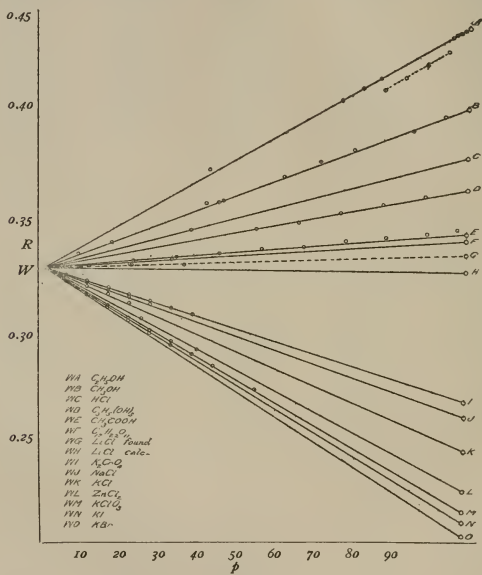
Fig. II.

specific refractions of pure solvent and solute; (2) those in which the experimentally determined specific refractions do not lie on this line. All of the solutes belonging to the first class are anhydrous, whereas the solutes of the second class either crystallize from solution with water of crystallization or are known to possess marked affinity for water. In plotting the data for hydrated solutes dotted lines have been employed.

For example, in Fig. IV., WD represents the calculated line for sulphuric acid, while the dotted line WK is that actually found.

In the case of cadmium iodide there is marked disagreement between the observed and calculated values of R_2 but
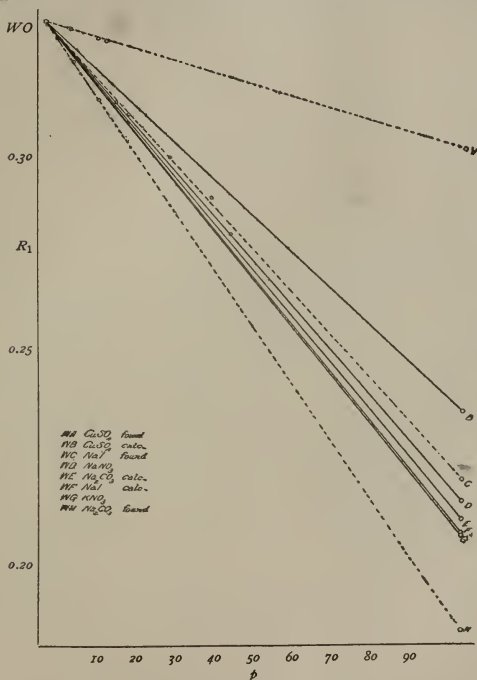
Fig. III.

we do not feel warranted in drawing any conclusions from this until the measurements have been repeated.

As has already been pointed out by Andrews,[1] there is a singular break in the refractive index-concentration curve

[1] *Loc. cit.*

for ethyl alcohol. This is also apparent in the specific refraction-concentration diagram. As Andrews has indicated, this break occurs at a concentration corresponding to the hydrate $3C_2H_5OH.2H_2O$.

In the tables the average value of R_2 has been tabulated for all of the anhydrous solutes studied, this average value be-

WA	n-C_3H_7COOH	
WB	$AlCl_3$	found
WC	$CaCl_2$	found
WD	H_2SO_4	calc-
WE	$AlCl_3$	calc-
WF	$CaCl_2$	calc-
WG	HNO_3	found
WH	$CuCl_2$	found
WI	$CuCl_2$	calc-
WJ	HNO_3	calc-
WK	H_2SO_4	found
WL	$CdCl_2$	found
WM	$CdCl_2$	calc-
WN	CdI_2	
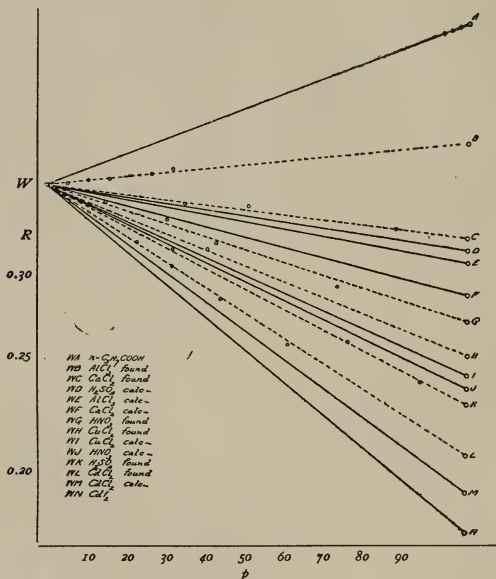
Fig. IV.

ing in good agreement with that calculated from the refractive equivalents of the constituent elements. In the case of ethyl alcohol this average value was obtained by excluding the four values which lie on the parallel dotted line shown in Fig. II., since this evidently does not refer to anhydrous alcohol.

In Table XXX. is given the value of the specific refraction as calculated from refractive equivalents for the anhydrous solute (R_a), for the hydrated solute (R_h), and also the experimentally determined value (R). In the fifth column the difference between the calculated and determined value is recorded.

Table XXX.

Solute.	R_a (calc.).	R_h (calc.).	R (found).	Diff.
NaCl	0.2649		0.2675	—0.0026
NaI.2H$_2$O	0.2136	0.2303	0.2263	+0.0040
NaNO$_3$	0.2211		0.2200	+0.0011
Na$_2$CO$_3$.10H$_2$O	0.2169	0.2692	0.1900	+0.0792
KCl	0.2486		0.2475	+0.0011
KBr	0.2079		0.1950	+0.0129
KI	0.2144		0.2195	—0.0051
KNO$_3$	0.2131		0.2200	—0.0069
KClO$_3$	0.2198		0.2075	+0.0123
K$_2$CrO$_4$	0.2722		0.2757	—0.0035
LiCl.2H$_2$O	0.3341	0.3184	0.3425	—0.0241
CaCl$_2$.6H$_2$O	0.2828	0.2913	0.3100	—0.0187
CuCl$_2$.2H$_2$O	0.2444	0.2561	0.2538	+0.0023
CuSO$_4$.5H$_2$O	0.2424	0.2632	0.3050	—0.0418
ZnCl$_2$	0.2294		0.2287	+0.0007
CdCl$_2$.2H$_2$O	0.1885	0.2067	0.2063	+0.0004
CdI$_2$	0.1698		0.1846	—0.0148
AlCl$_3$.6H$_2$O	0.2981	0.2989	0.3550	—0.0561
HCl	0.3889		0.3882	+0.0007
HNO$_3$	0.2381		0.2700	—0.0319
H$_2$SO$_4$	0.3041		0.2305	+0.0735
CH$_3$COOH	0.3525		0.3550	—0.0025
n-C$_3$H$_7$COOH	0.4123		0.4123	0.0000
CH$_3$OH	0.4122		0.4122	0.0000
C$_2$H$_5$OH	0.4506		0.4506	0.0000
C$_3$H$_5$(OH)$_3$	0.3738		0.3720	+0.0018
C$_{12}$H$_{22}$O$_{11}$	0.3491		0.3537	—0.0046

Reference to Table XXX. shows that there is approximate agreement between R_h and R for NaI.2H$_2$O, CuCl$_2$.2H$_2$O, and CdCl$_2$.2H$_2$O, but that for other hydrated solutes marked differences exist. For the three salts named above it is possible to calculate quite closely the number of molecules of water of crystallization from the specific refractions of solute and solvent.

Let Rm denote the molecular refraction of the solute, the molecular refraction being the product of the specific refraction of the solute, R, and its molecular weight m, and let n be the number of molecules of combined water.

Then

$$r = \frac{Rm + 5.4\,n}{m + 18\,n} \qquad (3),$$

where r is the specific refraction of the solute determined by experiment and 5.4 is the molecular refraction of water.

Solving (3) for n we have

$$n = \frac{(R - r)\,m}{18\,r - 5.4} \qquad (4).$$

Applying equation (4) to sodium iodide, cupric chloride, and cadmium chloride we find for n the values, 2.2, 2.0, and 2.4, respectively. Attempts to apply the equation to other solutes having a greater number of molecules of water of crystallization or having marked affinity for water, as sulphuric acid, have been unsuccessful, in several cases n being affected with a negative sign.

The results of this investigation may be summarized thus:

(1) Aqueous solutions may be divided into two classes:

(*a*) Those in which the specific refraction of the solute as calculated from its solutions agrees with its specific refraction as computed from the refractive equivalents of its constituent elements.

(*b*) Those in which the specific refraction of the solute as calculated from its solutions does not agree with the specific refraction as computed from refractive equivalents.

(2) All solutes belonging to division (*a*) are anhydrous; all solutes belonging to division (*b*) are hydrated.

(3) An attempt was made to derive a formula for calculating the degree of hydration, but as yet no satisfactory quantitative expression can be given.

We propose to continue the investigation of the relation of specific refraction to hydration.

ACTION OF RADIUM EMANATION ON SOLUTIONS OF COPPER SALTS.[1]

By Mme. Curie and Mlle. Gleditsch.

Ramsay and Cameron announced a year ago, in various publications, that they had observed the production of the alkali metals and of lithium in solutions of copper salts subjected to the action of radium emanation. They concluded that in the presence of the emanation the metal copper suffers a *degradation* into elements of the same family and of lower atomic weights: potassium, sodium, lithium.[2]

These important results attracted much attention and it seemed desirable to repeat the experiments in laboratories which possess a sufficiently large quantity of radium.

They carried out their experiments as follows: A solution of a copper salt (sulphate or nitrate) was placed in a glass bulb into which a considerable quantity of emanation was introduced and allowed to destroy itself spontaneously. Then the copper was removed, the solution remaining evaporated to dryness, and the residue examined. The same operations were carried out with a solution of the same copper salt but which had not been subjected to the action of the emanation. The experiments were repeated several times. The residue consisted principally of a sodium salt (with a little potassium and calcium); in the four experiments described, where the emanation was allowed to act on the solution, the presence of lithium was observed by means of the spectroscope; in the blank experiments the residue was appreciably smaller, and no lithium was detected. Ramsay and Cameron attempted to determine the amount of lithium present, and they concluded that the residue, which weighed 1.67 mg. for 0.27 gram copper employed (0.815 gram copper nitrate), contained about 0.00017 mg. lithium, while in the corresponding blank experiment the residue weighed only 0.79 mg.[3]

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[1] Compt. rend., **147**, 345 (1908).

[2] Nature July, 1907; J. Chem. Soc., Sept., 1907; Compt. rend., 1908; Arch. Genève, April, 1908; etc.

[3] This quantity of metallic lithium does not correspond to the amount indicated by the mixture of sodium and lithium salts which were employed for comparison, and there must be a typographical error which we have been unable to locate.

We have attempted to repeat the experiments with the greatest possible care. The experiment is, in fact, a delicate one and involves several sources of error, the most serious of which is the use of a glass vessel, as Ramsay himself pointed out.

Our preliminary experiments showed that it is extremely difficult to obtain chemical products free from lithium. It is found in distilled water, in almost all reagents; if a reagent which does not contain any is allowed to stand in a glass vessel, it will after a time show traces of the metal. The following experiment was carried out: Two hundred and fifty cc. of water which had been distilled from a platinum retort and kept in a platinum bottle left no visible residue when evaporated in a platinum dish, and the last drop resulting from the concentration did not give the lithium spectrum; but water obtained in the same way, when kept in a glass vessel for 24 hours, left, on evaporation, a small residue consisting principally of a sodium salt, but containing also a trace of lithium.

It seemed to us indispensable to replace glass by some other material. We found that it is equally dangerous to employ quartz, a material which Ramsay is now using, because commercial quartz vessels contain lithium. We treated a fragment of an opaque quartz vessel and a piece of transparent quartz tubing with hydrofluoric acid free from lithium; in the residue the presence of an appreciable quantity of lithium could be detected; transparent quartz contains much more than opaque quartz. We then decided to use platinum vessels.

The apparatus which we employed consists of a horizontal platinum cylinder, 7.5 cm. long and with an external diameter of 1.5 cm.; this cylinder is provided at one end with a small vertical platinum tube through which the solution can be introduced. The small tube has a platinum cover which protects the solution but is not water-tight. A glass tube provided with a side tube and stopcock is sealed on the outer side over the platinum tube. The solution is introduced into the apparatus by means of a platinum siphon and is re-

moved in the same way and never comes in contact with glass.

The water and acids necessary for the experiment were distilled in a platinum retort and kept in bottles made of the same metal; we had found, in fact, that all these reagents contained lithium, especially the sulphuric acid. After the purification described above, we were no longer able to detect the presence of lithium in the residue from the evaporation of 80 cc. of nitric acid, 25 cc. of sulphuric acid, 25 cc. of hydrofluoric acid, and 250 cc. of water.

As Ramsay pointed out, pure commercial copper salts contain appreciable quantities of lithium. We tried various processes of purification: repeated precipitation with hydrogen sulphide, electrolytic deposition of the copper, fractional crystallization; finally we used copper sulphate which had been recrystallized many times in a platinum vessel, pure water being used for each successive solution. This treatment is at first very efficacious, but on the other hand it is very difficult, if not impossible, to remove the last traces of lithium. When we discontinued the purification we could with great difficulty detect lithium in the residue from 50 grams of copper, but not at all in the residue from 2 grams of the salt.

The emanation was supplied by a solution containing 0.19 gram of radium (0.25 gram of radium chloride). It was first condensed in a spiral immersed in liquid air, then aspirated into the platinum apparatus. To determine with certainty the amount of emanation which was introduced, we measured the penetrating radiation of the apparatus by comparing it with that of a phial containing a known quantity of radium. For this purpose we employed a specially constructed condenser with large plates.

Two experiments, which were in all respects analogous, were performed. We introduced into the apparatus about 7 cc. of a solution of pure copper sulphate. The liquid had a relatively large free surface compared to its volume. The apparatus was then sealed in the flame. The emanation was introduced at various intervals; in order to insure its solution the liquid was stirred by inclining the apparatus, which was

placed in melting ice; this operation was frequently repeated. The weights of copper used were 0.26 and 0.14 gram, respectively. The whole amount of emanation introduced corresponded in both cases to the saturated emanation of 0.37 gram radium; the quantity which was destroyed in the apparatus was somewhat less; it corresponded to the saturated emanation of 0.27 gram radium. When the experiment was thought to be completed, the solution was transferred from the apparatus to a platinum crucible and a few drops of nitric acid were added. Into the crucible was introduced a platinum electrode, on which the copper was deposited. The solution freed from copper was evaporated to dryness in the crucible and the temperature raised just high enough to expel the sulphuric acid; the residue was dissolved in a few drops of water and treated with hydrogen sulphide to remove the traces of copper which were still present. The liquid was filtered through a little platinum funnel into a platinum lid of known weight and evaporated to dryness at a very low temperature. The small residue was weighed.

Seven cc. of a solution of pure copper sulphate which had not been subjected to the action of the emanation were treated in the same way. The residues finally obtained were examined in the spectroscope. In the experiments in which the emanation had been used, the residues weighed 0.0004 and 0.0005 gram, respectively, and in the blank experiments 0.0003 and 0.0002 gram.

We may mention that the quantity of copper employed is nearly the same as that used by Ramsay. The amount of emanation which we utilized is also approximately the same (1.85 cubic mm., according to Ramsay's basis of evaluation). Nevertheless, the residue finally obtained was much smaller.

The spectroscopic examination showed that this residue contained principally sodium and a little potassium; the presence of lithium could not be detected. An experiment made with mixtures of sodium and lithium sulphates showed that the red line of lithium could still be detected, although with difficulty, in a mixture containing 10,000 parts of sodium sulphate to 1 part of lithium sulphate, and that the same line

could easily be seen with a mixture containing 3,000 parts of sodium sulphate to 1 part of lithium sulphate. Consequently the quantity of the metal lithium which could be present was less than 0.000006 mg.

With the same quantities of copper and emanation, Ramsay and Cameron found 0.00017 mg. lithium. If, owing to a typographical error, this value should represent lithium chloride, the quantity of the metal lithium would still be equal to 0.00003 mg.

The residue which we obtained was, in every case, much smaller than that obtained by Ramsay and Cameron, and this probably results from the substitution of platinum for glass in our experiments. The differences in the weights of the residues obtained by us in the experiments in which the emanation had beed used and in the blanks is very small (0.1 to 0.3 mg.); it is probably due to the fact that, in the former, traces of foreign matter are introduced with the emanation. In the most satisfactory of Ramsay and Cameron's experiments, this same difference is equal to 0.88 mg., and we believe that it may be attributed to the more energetic action of the solution on the glass in the presence of the emanation.

The following control experiment was carried out: Into a solution of copper sulphate containing 0.27 gram of copper, we introduced a quantity of lithium sulphate corresponding to 0.00017 gram of lithium chloride; this solution was then treated in the same manner as in the experiments described above. With the residue finally obtained it was very easy to see the red lithium line, which proves that the lithium was not lost during the course of the experiment.

In conclusion, we may say that we have been unable to confirm the results of Ramsay and Cameron. It is evidently impossible to affirm that no trace of sodium or lithium was formed in the experiment; we believe, however, that the formation of these elements cannot be considered an established fact.

REVIEWS.

A COURSE OF PRACTICAL ORGANIC CHEMISTRY. By T. SLATER PRICE, D.Sc., PH.D., F.S.C., Head of the Chemical Department of the Birmingham Municipal Technical School; Formerly Senior Lecturer on Chemistry at the University of Birmingham, and DOUGLAS F. TWISS, M.Sc., A.S.C., Lecturer on Chemistry at the Birmingham Municipal Technical School. London, New York, Bombay, and Calcutta: Longmans, Green & Co. 1907. pp. 239. Price, $1.20.

This text-book is intended to meet the requirements of the "Board of Education" syllabus for Practical Organic Chemistry. The authors say: "We have endeavored to arrange the course so that the student will get a completely satisfactory practical acquaintance with organic chemistry." The preparations have been selected with care and the descriptions are clear. There can be no doubt that any student who conscientiously follows the course here laid down will acquire a good knowledge of the subject. Whether the knowledge will be "completely satisfactory" will depend upon what is expected.

In addition to the directions for preparations there are given many "tests" and schemes for the identification of compounds. Chapter XIV. treats of the determination of the molecular weight (1) by chemical methods, (2) by physical methods. Chapter XV. treats of special quantitative work; and Chapter XVII. gives a general scheme for the detection of an organic compound.

The book appears to be well adapted to the purposes for which it has been written.   I. R.

LABORATORY EXERCISES IN PHYSICAL CHEMISTRY. By FREDERICK H. GETMAN, PH.D., Lecturer in Physics, Columbia University, formerly Carnegie Research Assistant, Johns Hopkins University. Second Edition, Revised, First Thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1908. pp. 285. Price, $2.00.

The appearance of the first edition of this admirable laboratory manual was duly referred to in THIS JOURNAL.[1] The prompt appearance of the second edition shows that the book has been favorably received. Some additions have been made in this new edition, as is shown by the following lines taken from the preface: "The author would call attention to the insertion of a chapter on thermostats and to the enlargement of the chapters treating of electromotive force, solubility, and chemical dynamics.

"A brief outline is given of methods for the measurement

[1] **32,** 296 (1904).

of radioactivity, and several other chapters have been modified to conform with modern laboratory requirements."

The work presents a truly scholarly appearance, which is more than can be said of many scientific books. The reviewer must, however, object to the use of "foreward" in English. In the next edition, which will doubtless be quickly demanded, let us hope that the author will remove this trifling blemish.   H. C. J.

DIE ENTWICKELUNG DER LEUCHTGASERZEUGUNG SEIT 1890. Sammlung chemischer und chemisch-technischer Vorträge. Band XII., Hefte 7–8. Von DR. W. BERTELSMANN. Stuttgart: Ferdinand Enke. 1907. pp. 90. Price, 1.2 Marks.

As would be expected, the book deals largely with the apparatus employed, discussing first the horizontal retorts and the devices for mechanically charging and discharging them; this is followed by a description of the various inclined and vertical retorts and the coke ovens. About one-third of the book is devoted to the manufacture of water gas and mixed gases. Finally other methods of gas manufacture are discussed; the Dinsmore, the injection of tar and alcohol into the retorts, and the process of Sabatier in which methane is made by passing carbonic oxide and hydrogen over hot iron.

The statistics contained in the book are valuable and it will be of interest to all those having to do with the manufacture of gas.   A. H. GILL.

THE DATA OF GEOCHEMISTRY. By FRANK WIGGLESWORTH CLARKE, Washington: U. S. Geological Survey, Bull. 330. 1908. pp. 716.

The appearance of this work, bringing together the scattered information gathered by many investigators working with different ends in view, emphasizes the fact that there is developing another series of problems in a field lying between the well-marked sciences of chemistry and geology. The field demands the simultaneous application of the mental methods of exactness developed in chemical work and of convergent approximation necessary in the study of more or less irreducible complexes such as the earth studies furnish. It need not seem strange, therefore, if summaries like the present one occasion misunderstanding or inappreciative criticism on the part of workers accustomed to employ but a single viewpoint. The work is issued, not as an exhaustive monograph on the subject, but rather as a critical summary and guide to the literature. The purpose appears to be the collection of the data, the formulation of problems, and the restatement of old facts in modern terminology. To this

end the author has compiled the chemical data concerning the earth as a whole, its waters—oceanic, lacustrine, and fluviatile; its rocks, their minerals, origin, and alteration; the metallic ores; and the natural hydrocarbons. The wealth of material brought together is made accesible by an excellent index of fully 5000 entries. The summaries are clear, concise, and critical, and the most recent literature is unusually well represented.

Among the many interesting topics discussed, attention may be called to the large amount of recent work in the study of the physical-chemical conditions surrounding the formation of the igneous rocks, their magmas, minerals, and alterations. The summaries seem to indicate that the investigators now generally accept the view that rock magmas are solutions under great pressures and at high temperatures, behaving essentially like other solutions; that they conduct electricity and may be at least partially ionized. There is, however, little knowledge or agreement as to the composition of the ions or the conditions especially helpful to dissociation. It is also agreed that in some instances, at least, the components of the magmas form eutectics but these are unknown or unproven. The components are probably more than three and each is a complex silicate. Moreover, the composition of the eutectics appears to be different at different temperatures and pressures and to be in some way variable with the bulk composition of the magma.

It likewise is generally accepted that the chemical composition of magmas possess certain characteristic differences and that the rocks produced from a given magma may differ widely in composition while retaining certain common characteristics. To explain these phenomena many hypotheses have been proposed and these may be grouped as follows:

Differences in composition due to mixing:

    a. Two or more magmas of different composition.

    b. Magmatic assimilation of the rock intruded.

Differences in composition due to the separation of a homogeneous magma into parts through

    a. Concentration of the dissolved substances in the cooler parts of the reservoir.

    b. Separation of the magma into layers by liquation.

    c. Separation by fractional crystallization, gravitational adjustment and refusion due to

        (1) Variation in pressure and temperature, or

        (2) Excess of components over eutectics.

The widely divergent views are held by prominent workers to-day but the drift of opinion appears to be that all causes

may be competent and that fractional crystallization is the most efficient. No final solution is likely to be reached without a great increase in knowledge of solutions at high temperatures and under high pressure, their components, eutectics, and conductivities; and the conditions, chemical and physical, determining the formation of a given silicate complex from a silicate melt.   E. B. MATHEWS.

LEAD REFINING BY ELECTROLYSIS. By ANSON GARDINER BETTS. New York: J. Wiley & Sons. 1908. pp. ix + 394. Price, $4.00.

In the desilverization of argentiferous lead the Parkes process has so far occupied the whole field, if we except the Luce-Rozan process in operation some twenty years ago at Eureka, Nev. The different attempts at electrolytic refining all proved a failure until the invention of the Betts process, in which an aqueous solution of lead fluosilicate acidified with hydrofluoric acid is the electrolyte. From the argentiferous lead forming the anode, copper, antimony, bismuth, arsenic, silver, and gold go into the anode slime; zinc, iron, nickel, and cobalt go into solution; and lead and tin are deposited on the lead cathode. In the presence of tin this would have to be removed by the usual fire process before electrolysis.

The present book is a record of the large amount of research, mainly by the author, which preceded the erection of a working plant to make a commercial test; a discussion of the practical features; and a brief description of the two plants in operation.

The first chapter reviews critically the different electrolytes that have been recommended for refining lead and gives full details regarding the successful acid lead fluosilicate. The question of slime treatment is discussed very elaborately and gives a variety of methods. The reason for this probably is the fact that this part of the process has not yet been worked out to complete satisfaction. The space given to the electrolytic refining of doré silver is a great deal too small, even if it is foreign to the main purpose of the book. Discussions of practical details of construction, of operation and of cost forms a most valuable chapter. The descriptions of the works at Trail, B. C., and Grasselli, Ind., are probably as complete as business considerations make this possible at present. Whether the new process will be able to compete with the established Parkes process, as is held by the author, is still an open question.

Taking the book as a whole, it is written by a man who is a master of his subject, and who has tried to the best of his

ability to give an unprejudiced account of all that can be made known at present about the only successful method of refining argentiferous lead electrolytically.   H. O. Hofman.

Practical Methods for the Iron and Steel Works' Chemist. By J. K. Heess, Ph.C., Chief Chemist for the Carnegie Steel Co.   Easton Pa.: The Chemical Publishing Co.   pp. 60.

This book contains descriptions of the methods used by the author in the analysis of iron and steel, and all the various materials employed in their manufacture.

The methods are those ordinarily adopted in large plants and are selected more for the facility and speed of their execution than for the accuracy of the results obtained by their use.

In his introduction, the author states that the work is intended for the inexperienced chemist, and to accustom him to their use, he mars the appearance of his text by the general use of formulae and symbols. For those who are not only inexperienced but ignorant, he provides a table with the names and formulae of the various reagents and salts. The reactions on which the methods are based are, however, omitted, probably to avoid mental confusion in the reader, who, being supposed to have no knowledge of the principles of chemistry, can follow the directions with an easy mind.

The substance of the text is entirely in keeping with its appearance. The ordinary rules of English grammar are generally disregarded. The article and the impersonal pronouns are usually omitted, while the use of the passive form of the indicative and the imperative in the same sentence is not uncommon. Occasionally this disregard of rules is actually misleading, as in the sentence "a slag sample so kept is not reliable only for a short time." Such expressions as "let stand," "take about to dryness," "let boil," "doing steel," "doing a manganese," are found on every page, while in one instance, the neophyte is warned not to make a solution "too neutral."   A. A. Blair.

AMERICAN

CHEMICAL JOURNAL

THE FRACTIONATION OF CRUDE PETROLEUM BY CAPILLARY DIFFUSION.

By J. E. Gilpin and M. P. Cram.

When, in process of refinement, black vaseline is filtered through warm dry fuller's earth the first product is an oil perfectly liquid at ordinary temperatures, while the succeeding portions are progressively more viscous until quite hard vaseline is obtained. This observation, that a fractional separation of oils in vaseline had been effected, suggested to D. T. Day that a like result might be obtained with crude petroleum. He applied this method to a sample of the green crude petroleum from the "third sand" of Venango County, Pennsylvania, and found that light products, chiefly gasoline, first appeared when such crude oil was allowed to filter down through a long glass tube filled with granulated or powdered fuller's earth.[1]

Following this, a more elaborate system of specially constructed funnels, similar to those used by the refiners of vaseline in testing the comparative value of various fuller's earths, was used. The results of this work were briefly summarized in a paper upon the ability of petroleum to migrate in the

[1] P. Am. Phil. Soc., **36**, No. 154, 1897.

earth.[1] Engler later verified these results and showed that the separation was mechanical and that no oxidation was effected in the process. Day next used a large closed funnel of galvanized iron holding about one hundred pounds of fuller's earth. When crude petroleum was dropped slowly and regularly into this, quite light oils at first, followed by the usual succession of heavier oils, were obtained. As it was evident from this work that much of the oil passed through crevices without any change he tried the effect of reversing the route of the oil and of allowing it to diffuse upward through a tube packed tightly with fuller's earth. In such a tube the lighter constituents rose much more rapidly than the more viscous oils so that by separating the fuller's earth from different sections of the tube and displacing the oil by water, quite different oils were obtained from the upper and lower parts of the tube.

By using several tubes and uniting oils of the same specific gravity, oils of different grades can be collected in sufficient quantity to be fractionated again, and the process continued until oils result which are not altered by further passage through tubes filled with fuller's earth. At the suggestion and with the coöperation of Day, we have taken up this problem, with the results stated below.

The tubes used first were three feet long and one and one-eighth inches in diameter. They were closed at the lower end with corks, along the sides of which grooves had been cut, the top of the cork being covered with a bit of cotton cloth to prevent the earth from sifting out of the grooves. Such tubes filled with fuller's earth[2] were placed with their lower ends in an open dish of petroleum and the oil was allowed to rise.

At room temperatures (18°–22° C.) and atmospheric pressure, the rate of rise of crude petroleum in a tube filled with fuller's earth was very slow. In seven days the oil ascended but 73 cm. in one tube, while ten days in one case and seven in another were required for it to rise 59 cm. To study the

[1] Trans. Petroleum Congress, Paris (1900).
[2] The fuller's earth used in this work was kindly furnished by the Atlantic Refining Co., of Philadelphia.

effect of heat, a glass tube about three feet long and $1\frac{1}{8}$ inches in diameter was filled with earth and placed in a bottle holding about two liters of oil, and the whole heated by an electric stove by means of which temperatures considerably above those of the room could be maintained day and night. The temperature of the tube was kept between 40° and 70° for three days, in which time the oil rose 54.7 cm. in the tube; in another tube packed in all ways like the former but kept at room temperature (about 20°), the oil rose 46 cm. in the same length of time. With two tubes in which the earth was packed much less compactly, the time required for the oil to rise 54 cm. was four days for the tube at room temperature and two days for the one at 50° to 80°.

The rate of rise evidently was but little affected by heat, at least within this range of temperature, and higher temperatures could not be used without loss of the more volatile constituents of the oil.

The next attempt at increasing the rate of rise of the oil consisted in applying diminished pressure to the top of the tube, which reduced the time required for the oil to reach the top of a tube five feet long from several weeks to seventeen hours. If diminished pressure is continued after the oil has reached the top, provided the oil is not exhausted in the reservoir at the bottom, oil will be drawn over from the top of the tube. The specific gravity of the oil thus collected steadily rises as it comes over. The samples so obtained, however, stand under very low pressures for some time, which may cause a loss of their more volatile constituents. This suggested applying increased pressure to the oil in the reservoir rather than diminished pressure to the top of the tube, and an iron bomb, like those used for the transportation of mercury, was fitted with an iron pipe seven feet long to contain earth and a side arm at the bottom of the bomb to which a water column could be attached.

The bomb, which held about two liters, could be partly filled with petroleum and the pipe containing the earth screwed into the top. The side arm which opened into the bottom of the bomb could then be connected with the water pressure

so that the lower part of the bomb was filled with water which drove the petroleum upwards. The oil obtained at the top, however, was fractionated no further nor in any larger amounts than when the oil was not allowed to emerge from the top of the tube. The difficulty of setting up such a pressure apparatus with tight connections, as well as the range of pressure required—a column of water seven feet high being too great when the oil was just starting up the tube while a column thirty feet high was insufficient when it was near the top—made the use of this method impracticable.

To use diminished pressure, the earth in the tubes must not be packed so hard that the air just above the oil cannot be drawn through the earth above, nor must the earth be packed so loosely that the oil will rise as in a vacuum. The right degree of hardness is obtained by filling about a foot of the tube at a time and packing that much earth as hard as possible with a wooden rod tipped with a rubber stopper. If the tube, when pounded upon the floor, rings in the hand, the earth is apt to be packed too closely. Packing tubes may be much facilitated by filling several at once with a separate ramrod for each. By allowing a few minutes to elapse between successive liftings of the ramrod, in order that the air may escape and the fuller's earth settle, much labor is avoided.

The fuller's earth was first heated in shallow iron pans until it ceased to form geysers when stirred. The earth must be thoroughly cold before it is packed into tubes or the contraction is sufficient to allow the oil to run up the tube immediately when the air is exhausted.

The lower end of the tube is best closed with a cork with six or seven grooves cut along the side, and the inner end covered with a bit of cloth to keep the earth from sifting out of the grooves. At the top of the tube a bit of cotton waste below a rubber stopper will prevent any earth from being drawn up when the air is exhausted.

The tubes used first were three feet long and one and one-eighth inches in diameter and of glass. Much trouble was experienced on account of their breaking, not when in ser-

vice, but soon after they had been used. This was thought to be due to the age of the tubing, but the same happened with new tubes five feet long and one and one-fourth inches in diameter. Thinking that the iron scraper used to remove the earth from the tubes might be the cause, we tried a scraper made entirely of wood, but this did not decrease the breakage, it being nothing unusual on going to the laboratory in the morning to find that half of the tubes which had been emptied the day before were cracked.

It had been considered necessary to use tubes of glass in order that the height to which the oil had risen might be seen and that in removing the oil from the middle of the tube it might be scraped out to a sharp dividing line, since the level to which the oil has risen is the point from which all measurements should be made of sections into which the tube is to be divided. Tin tubes were used later to avoid the trouble experienced with glass tubes. These tin tubes were emptied by shaking the earth from the bottom into four thirty-centimeter cylinders of the same diameter as the tube, these cylinders being made of two curved pieces of tin held together by a cap at one end and a ring at the other. The cylinders containing the contents of the tube could be opened lengthwise and the earth divided into any desired lengths. Two glass tubes five feet long and one and one-fourth inches in diameter were set up in the same dish of petroleum with ten or twenty tin tubes of the same diameter, and five and one-half feet long, and when the oil stood at the top of the glass tubes the tin ones were opened. Glass tubes, of course, can be emptied as well as tin ones by shaking the contents from the bottom, and no more tubes broke after this method was adopted.

The level to which the oil will rise can be regulated by the amount of oil in which the tube is placed, and in the later work the adoption of this method did away with the use of glass tubes entirely. With nine hundred and fifty cc. the oil will rise to within 20 to 35 cm. of the top of a tube one and one-fourth inches in diameter and five and one-half feet long.

When the oily earth has been removed from the tube, the

oil may be separated by adding water. In the first experiments enough water was added to form a very thin mud which was thoroughly stirred by a small propeller driven by a water motor. The mixed earth, oil, and water were then poured into a large separating funnel and allowed to stand several minutes until the oil had collected at the top. The earth and water could then be drawn off and the pure oil left.

It was found later, however, that if less water is added to the earth as removed from the tubes, after standing a few minutes all the water will pass into the earth and this will be accompanied by the liberation of oil. Oil so liberated can then be poured off directly from the earth without the labor of churning. When water first begins to liberate oil, the earth is granular, whereas when more water has been added and the last of the oil recovered the earth has the consistency of a thin paste which will flow when the dish is inclined.

All the oil from the same section of a tube is of the same color irrespective of whether it is the first oil to separate when water is added or whether it does not separate until the last. It was assumed at first that all such oil which was obtained from the same section of earth had the same specific gravity whether it was the first or last replaced when water was added, but this was found later not to be the case.

The first oil to be collected, if taken in sufficiently small volume, is slightly heavier than the next portion. If too much is included in the first sample this will not be the case. Beginning with the second sample the successive portions of oil steadily increase in specific gravity, this gradual addition of water affording another means of fractionation in addition to the separating power of the earth. Both of these methods of separation have been combined in this investigation. The earth must be thoroughly mixed after each addition of water so that the layer of wet earth shall not isolate the oily earth from the water added.

The petroleum used was a dark green oil from Venango County, Pennsylvania, of specific gravity 0.810. When

950 cc. of this were drawn upwards in a tin tube five and one-half feet long the separation shown in Table I. was obtained.

Table I.—Single Tubes in the Crude Petroleum.

	(1)		(2)		(3)	
Time required	23.5 hrs.		17.5 hrs.		17.5 hrs.	
Distance from top of tube to oil when opened ...	31 cm.		28 cm.		28 cm.	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A, 8 cm. at top...	0.796	42	0.8012	30	0.8022	18
B, next 8 cm.....	0.808	45	0.804	37	0.803	35
C, next 18 cm....	0.8125	75	0.807	47	0.8075	66
	0.8137	24	0.809	22	0.810	25
D, next 30 cm....	0.815	130	0.8125	148	0.812	140
E, next 35 cm....	0.818	170	0.8185	190	0.8175	145
F, rest...........	0.8205	125	0.823	100	0.821	105
		611		574		534

The oil from section C was collected in two portions, the second being obtained by the addition of more water after the first lot of oil was poured off. Although 950 cc. of crude petroleum were used in each case, it will be noticed that the amount of oil recovered was much less than that. When several tubes were worked up together, in one case 9070 cc. of crude petroleum yielded 5951 cc. of oil, and in another case 8915 cc. gave 5415 cc.

To collect a sufficient quantity of oil several tubes were placed in the same vessel containing the petroleum, two of the tubes being of glass and the rest of tin. When the oil had reached the top of the glass tubes they and the tin ones were opened, and the earth from the same level in all the tubes was, mixed in tin pails. The oil was then liberated in several successive fractions by the addition of successive amounts of water. If the earth had been thoroughly mixed after each addition of water the various oils from the same lot of earth would increase regularly in specific gravity, instead of showing the variations which in many cases they do; *e. g.*, the first oil to be displaced by water in D and E of (4), in Table II., with so large volume, would not have been heavier than the suc-

ceeding oils if the water and earth had been thoroughly mixed before the oil was poured off. If we were to repeat the work, instead of using one common reservoir for all the tubes, we would use a separate reservoir for each tube, and open the tube when the oil in the reservoir was exhausted. This would do away with the use of glass tubes entirely, besides insuring that the level of the oil in each tube when opened would be practically the same. If a common reservoir is to be used the tubes should all be packed with practically the same degree of hardness if the oil is to ascend in all with equal rapidity, since the ascent in all tubes is checked at the same time, *i. e.*, when the oil in the reservoir is exhausted.

Diminished pressure was obtained by use of a Chapman water pump which reduced the pressure to from five to twelve cm. mercury when connected with a system of tubes. In the earlier work the pump was not run through the night. This is the reason why these lots of tubes required so much more time.

The earth from a tube was divided into six sections, the level to which the oil had ascended in the tube being taken as the point to be measured from. A, the top section, includes the eight cm. next the top; B, the next eight cm.; C, the next eighteen; D, the next thirty; E, the next thirty-five; while F includes what earth is left. F varies, of course, depending upon the height to which the oil has risen. In fractionating the crude petroleum in bulk, F was usually discarded since it was so viscous that it was deemed impossible to pass it through earth again. Records from several lots of tubes are given in Table II. The specific gravity was measured with a Westphal balance, the temperature being in every case exactly 20° C. While the fourth decimal place is not to be taken as strictly accurate, yet it is considered worth while to record it as giving a nearer approach to the truth than would result from the use of only three decimal places.

Table II.—First Fractionation of Crude Petroleum.

Tubes. Distance from level of oil to top of tube in cm.[1] Hrs. required.	(4) 2 glass, 8 tin. Glass, 0, 15. Tin, 40, 15, 24, 22, 28, 19, 24, 32. 54		(5) 2 glass, 7 tin. Glass, 0, 6.5. Tin, 26, 28, 18, 15, 28, 12, 24. 24		(6) 2 glass, 8 tin. Glass, 0, 12. Tin, 30, 28, 22, 30, 13, 12.[2] 54	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8015	50	0.804	100	0.805	65
	0.8005	350	0.8055	190	0.805	200
B	0.807	260	0.8085	220	0.807	140
	0.810	190	0.811	120	0.8097	125
C	0.809	100	0.8097	430	0.810	390
	0.809	400	0.8122	300	0.8135	380
	0.810	225				
	0.8115	260				
D	0.815	425	0.813	530	0.8133	610
	0.8145	625	0.8135	600	0.816	325
	0.8175	460	0.816	200	0.8175	435
					0.825	125
E	0.816	440	0.8162	480	0.816	850
	0.815	400	0.8162	725	0.8195	260
	0.821	830	0.819	390	0.821	330
					0.827	325

	(7) 2 glass, 7 tin. Glass, 0, 7. Tin, 25, 26, 23, 26, 28, 20, 28. 84		(8) 2 glass, 7 tin. Glass, 0, 5. Tin, 16, 34, 28, 15, 18, 23, 10. 48		(9) 2 glass, 7 tin. Glass, 8. 5, 15. Tin, 58, 31, 60, 40, 16, 53, 16. 117		(10) 2 glass, 9 tin. Glass, 0, 8. 5, Tin, 40, 32, 36, 26, 27, 27, 20, 25, 18. 84	
A	0.800	200	0.798	130	0.8025	175	0.7995	200
	0.802	115	0.801	130	0.8037	120	0.8037	160
							0.806	23
B	0.8042	200	0.803	155	0.8042	180	0.8085	125
	0.8048	200	0.8045	230	0.8078	215	0.810	275
							0.8112	23
C	0.808	330	0.8072	430	0.809	300	0.810	350
	0.8078	430	0.808	275	0.8095	440	0.812	525
	0.811	95	0.808	225	0.8127	100	0.8135	150

[1] The glass tubes are five feet long, the tin tubes five and one-half feet. Both are one and one-quarter inches in diameter.

[2] Record of distance lost for two tin tubes.

Table II. (Continued).

(7) 2 glass, 7 tin. Glass, 0, 7. Tin, 25, 26, 23, 26, 28, 20, 28. 84		(8) 2 glass, 7 tin. Glass, 0, 5. Tin, 16, 34, 28, 15, 18, 23, 10. 48		(9) 2 glass, 7 tin. Glass, 8, 5, 15. Tin, 58, 31, 60, 40, 16, 53, 16. 117		(10) 2 glass, 9 tin. Glass, 0, 8, 5. Tin, 40, 32, 36, 26, 27, 27, 20, 25, 18. 84	
D 0.812	425	0.8117	420	0.812	390	0.8148	440
0.812	625	0.812	580	0.8137	400	0.8175	700
0.814	360	0.822	250[1]	0.8145	300	0.817	370
		0.8145	300	0.8155	200	0.817	200
		0.8177	42				
E 0.8172	240	0.8135	390	0.818	340	0.8197	315
0.816	650	0.814	560	0.8197	240	0.8215	720
0.8162	660	0.8248	390[1]	0.818	290	0.8223	570
0.8195	300	0.817	230	0.818	350	0.821	215
		0.821	42				

(11)[2] 2 glass, 8 tin. Glass, 0, 4. Tin, 0, 0, 0, 0, 20, 17, 7, 5. 39		(12)[3] 2 glass, 6 tin. Glass, 7, 13. Tin, 32, 19, 32, 35, 48, 29. 60		(13)[4] 2 glass, 9 tin. Glass, 2, 2.5. Tin, 17, 10, 11, 22, 16, 29, 8.5, 5, 5, 14. 20		(14) 2 glass, 9 tin. Glass, 0, 0. Tin, 20, 20.5, 13.5, 15, 14.5, 19, 8, 12, 14. 16.5	
A 0.799	80	0.798	150	0.8015	110	0.798	225
0.802	180	0.801	140	0.8055	40	0.8005	110
				0.8028	125	0.8015	80
				0.8033	100		
B 0.807	200	0.8022	160	0.802	230	0.8015	210
0.8115	140	0.806	105	0.8072	60	0.804	150
		0.8072	20	0.8085	50	0.8058	120
				0.8075	75		
C 0.810	300	0.807	400	0.806	340	0.8048	500
0.811	490	0.809	200	0.808	220	0.8065	385
0.8145	175	0.8115	60	0.8072	320	0.8075	225
				0.8097	150		

[1] These fractions stood uncovered on top of the earth overnight and consequently were exposed to considerable evaporation.

[2] During the night oil was drawn entirely through and out at the top of five tubes which were lost.

[3] Three other tubes were set up with these but when opened the oil in these was 81, 81, and 90 cm., respectively, from the top, so they were discarded. The unevenness between the tubes was probably caused by using in some of them earth which was not entirely cold.

[4] Beginning with lot (13) the pump was run continuously day and night.

Table II. (Continued).

	(11)[1] 2 glass, 8 tin. Glass, 0, 4. Tin, 0, 0, 0, 0, 20, 17, 7, 5. 39		(12)[1] 2 glass, 6 tin. Glass, 7, 13. Tin, 32, 19, 32, 35, 48, 29. 60		(13)[1] 2 glass, 9 tin. Glass, 2, 2.5. Tin, 17, 10, 11, 22, 16, 29, 8.5, 5, 5, 14. 20		(14) 2 glass, 9 tin. Glass, 0, 0. Tin, 20, 20.5, 13.5, 15, 14.5, 19, 8, 12, 14 16.5	
D	0.8133	450	0.811	400	0.809	400	0.810	500
	0.8133	530	0.8097	420	0.8135	250	0.810	660
	0.816	290	0.811	290	0.8115	680	0.810	650
	0.8142	250	0.815	60	0.812	650	0.812	260
E	0.8172	400	0.815	260	0.813	400	0.8135	470
	0.818	520	0.8148	510	0.818	285	0.8155	530
	0.819	405	0.815	400	0.8167	700	0.8155	700
	0.8175	370	0.817	100	0.8167	805	0.8162	680

	(15) 2 glass, 9 tin. Glass, 0, 10. Tin, 32, 31, 23, 23, 24, 26, 9, 16, 14. 16.75		(16) 2 glass, 9 tin. Glass, 0, 5. Tin, 24, 19, 16, 15, 17, 23, 17, 4, 2. 16.5		(17) 1 glass, 9 tin. Glass, 14. Tin, 8, 27, 13, 6, 8, 0, 0, 0, 0. 17	
A	0.800	300	0.800	125	0.804	240
	0.805	95	0.8025	200	0.8055	120
			0.8028	80	0.8085	23
B	0.802	300	0.8042	245	0.812	220
	0.808	90	0.8065	100	0.812	155
	0.8055	120	0.810	110	0.8127	45
C	0.8065	800	0.8085	230	0.814	500
	0.810	350	0.8085	600	0.8125	450
			0.8115	210	0.815	40
D	0.8112	600	0.8117	435	0.814	540
	0.8142	525	0.8135	650	0.814	670
	0.8122	680	0.8137	370	0.8145	350
	0.8155	200	0.8148	350		
E	0.8145	740			0.817	740
	0.820	400	see		0.8172	750
	0.818	400	below			
	0.817	820				

[1] Foot-notes on preceding page.

Table II. (Continued).

	(18)[1]				(19)[1]			
	2 glass, 9 tin. Glass, 8, 5. Tin, 17, 2, 15, 19, 12, 22, 21, 0, 0.		2 glass, 9 tin. Glass, 14, 17. Tin, 30, 42, 39, 28, 35, 33, 42, 30, 42. 21.5		2 glass, 9 tin. Glass, 0, 0. Tin, 17, 11, 5, 18, 12, 15, 13, 18, 11. 23		2 glass, 8 tin. Glass, 0, 9. Tin, 13, 12, 15, 19, 11, 13, 26, 23	
A	0.8005	425			0.806	200		
	0.8005	225			0.804	300		
	0.8015	190			0.8085	180		
B	0.803	320			0.8055	290		
	0.803	320			0.8072	175		
	0.8042	200			0.809	175		
	0.8055	75			0.807	200		
C	0.8078	475			0.809	570		
	0.8078	680			0.8097	930		
	0.808	500			0.8135	140		
	0.8085	200			0.813	100		
	0.8095	170						
	0.8105	150						
D	0.8117	420	0.8122	500	0.8128	560	0.8128	475
	0.8117	680	0.8125	500	0.813	725	0.813	740
	0.813	660	0.814	350	0.815	400	0.8185	180
	0.8155	90	0.817	40				
E	0.8158	1450			0.816	930		
	0.8158	1000			0.816	930		
	0.8165	420			0.8165	460		
	0.8175	350			0.8185	400		
	0.8187	500			0.8185	520		
					0.820	200		

To study further the fractionation on addition of water, E from lot 16 was collected in fourteen fractions. The weight of the earth impregnated with oil before any water had been added was 13.5 pounds, while the weight of the earth containing all the water added, but minus the oil, was 17.5 pounds. The earth was placed in a galvanized iron garbage pail and the water stirred in with an iron paddle. When the first portion of oil was liberated the mass was of the consistency of bran, but as more water was added it turned to a fluid paste. When water was added and the pail inclined, oil

[1] (18) and (19). Two reservoirs of crude oil were used but the earth from all 22 tubes was worked up together. Grade D from all 22 tubes was first united and then, for convenience in working, divided into two portions.

would continue to drain for half an hour or longer before the addition of more water became necessary. The oil which was liberated by one lot of water, therefore, could be collected in several portions, and this was done to see whether the oil which comes off immediately after the addition of water is the same as that which drains later. The fractions included within the brackets were liberated by one addition of water.

	Sp. gr.	cc.			Sp. gr.	cc.
I............	0.821	25	IV........	{ 0.8208	575
				{ 0.8222	55
II..........	{ 0.818	70	V........	{ 0.824	170
	{ 0.818	70		{ 0.828	16
	{ 0.8193	250	VI........	{ 0.827	95
III........	{ 0.818	395		{ 0.830	45
	{ 0.818	350			
	{ 0.818	460			
	{ 0.820	60			

This phenomenon of a first fraction of higher specific gravity than the ones immediately following occurs regularly if the proper amount of water is added to liberate a first fraction of small enough volume. As the volume of the fraction first obtained becomes larger its specific gravity approaches nearer to that of the second fraction, and falls below it if its volume is made too large.

The range of specific gravity covered by this first fractionation of the crude petroleum of sp. gr. 0.810 was from 0.800 to 0.830. Oils of the same specific gravity and of the same grade were united and the products chilled and filtered to remove all the dissolved paraffine possible. The oils were chilled and filtered out of doors during the last of December when the thermometer stood at about 4° to 8° C. Lower temperatures would not only throw paraffine out of solution but would cause the whole oil to thicken as well. The oils were filtered through large plaited filters of drying paper, 24 hours or more often being required for a filter to empty completely. The lighter oils in grades A and B deposited no paraffine. The heavier grades deposited sometimes as much as 10 per cent of their weight, accompanied often by a slight change in specific gravity.

When these oils were filtered through earth again they behaved as shown in Table III. Nine hundred and fifty cc. were used in each tube, and for many tubes this amount of oil of the same grade (A, B, C, etc.) and of the same specific gravity was available. In some cases, however, it was necessary to unite oils of the same grade but which differed slightly in specific gravity. These differences never exceeded 0.0015. All cases in which this was done are marked *. The tube was divided into five sections. A, as before, is the top 8 cm., B the next 8, C the next 18, D the next 30, and EF the rest.

Table III.—The Second Fractionation.

	(20) A 0.8015 Sp. gr.	cc.	(21) A 0.806 Sp. gr.	cc.	(22)* B 0.805 Sp. gr.	cc.	(23) B 0.8055 Sp. gr.	cc.
A	0.8012	36	0.8038	45	0.7997	50	0.8005	45
B	0.800	44	0.8035	48	0.802	50	0.8033	48
C	0.8012	68	0.8035	78	0.8055	108	0.805	115
	0.8027	35	0.8052	28				
D	0.8022	170	0.805	160	0.8063	175	0.8063	180
EF	0.8047	330	0.807	320	0.808	260	0.8085	260
		683		679		643		648

	(24) B 0.8065 Sp. gr.	cc.	(25) B 0.809 Sp. gr.	cc.	(26)* B 0.8105 Sp. gr.	cc.	(27)* B 0.812 Sp. gr.	cc.
A	0.8077	38	0.8013	45	0.8075	38	0.8105	42
B	0.807	50	0.805	50	0.8085	50	0.8105	42
C	0.808	80	0.807	75	0.8105	100	0.8085	73
			0.810	30			0.810	22
D	0.8092	160	0.8095	180	0.8125	160	0.8115	140
EF	0.8115	300	0.8115	350	0.8135	275	0.8145	250
		628		730		523		569

	(28) C 0.8095 Sp. gr.	cc.	(29) C 0.810 Sp. gr.	cc.	(30) C 0.811 Sp. gr.	cc.	(31)* C 0.811 Sp. gr.	cc.
A	0.805	52	0.8035	40	0.8005	50	0.803	50
B	0.8065	52	0.808	40	0.809	38	0.808	55
C	0.8085	70	0.810	75	0.812	115	0.813	105
	0.811	28	0.8115	30				
D	0.811	160	0.8115'	140	0.813	175	0.8135	180
			0.8135	40				
EF	0.813	350	0.813	350	0.8145	310	0.8155	300
		712		715		688		690

Table III. (Continued).

	(32) C 0.8115		(33) C 0.813		(34)* C 0.8135		(35)* C 0.8135	
A	0.806	45	0.8072	20	0.803	42	0.8025	35
B	0.807	35	0.811	35	0.810	53	0.8077	35
C	0.810	60	0.812	70	0.813	100	0.8135	100
	0.812	33	0.813	25				
D	0.812	70	0.8145	90	0.815	150	0.8145	160
	0.813	97	0.815	80				
EF	0.813	103	0.8155	200	0.817	300	0.817	325
	0.8135	105	0.8155	125		—		—
	0.813	50	0.818	35		645		655
	0.813	47		—				
	Unused,	63		680				
		—						
		708						

	(36) C 0.815		(37)* C 0.8155		(38)* C 0.8155		(39)* C 0.8165	
A	0.805	43	0.8053	50	0.808	40	0.808	50
B	0.8105	40	0.812	45	0.8095	50	0.8145	50
C	0.814	98	0.816	103	0.8135	100	0.816	82
D	0.815	155	0.8175	160	0.817	165	0.8175	125
EF	0.817	280	0.819	310	0.819	290	0.820	310
		—		—		—		—
		616		668		645		617

	(40)* D 0.8135		(41) D 0.814		(42) D 0.814		(43) D 0.814	
A	0.8095	45	0.8045	30	0.806	32	0.806	25
B	0.8085	45	0.8115	45	0.811	45	0.8097	30
C	0.811	95	0.8135	75	0.813	92	0.814	50
			0.8165	28				
D	0.8155	165	0.818	140	0.8175	140	0.8157	145
EF	0.817	320	0.821	300	0.8195	310	0.8175	400
		—		—		—		—
		670		618		619		650

Table III. (Continued).

	(44) D 0.814		(45) D 0.814		(46) D 0.8145		(47) D 0.815	
A	0.8008	45	0.800	50	0.808	45	0.800	42
B	0.8077	50	0.8065	55	0.8115	40	0.807	47
C	0.814	103	0.8125	100	0.8135	65	0.814	110
					0.8155	30		
D	0.8175	160	0.816	160	0.817	105	0.816	150
					0.818	58		
EF	0.819	310	0.817	300	0.8195	180	0.819	330
		668		665	0.8202	120		679
					0.821	53		
						696		

	(48) D 0.815		(49) D 0.8155		(50) D 0.8155		(51) D 0.8155	
A	0.810	37	0.8045	40	0.8105	45	0.8058	40
B	0.805	47	0.811	48	0.8148	47	0.810	40
C	0.812	105	0.815	98	0.810	100	0.8132	60
							0.8145	50
D	0.817	160	0.8185	160	0.815	140	0.8172	75
							0.8188	55
							0.8188	38
EF	0.819	300	0.820	310	0.819	400	0.820	38
		649		656		732	0.819	100
							0.8208	30
							0.8208	45
							0.8208	30
							0.8208	95
							Unused,	40
								736

	(52) D 0.816		(53)* D 0.816		(54) D 0.8165		(55) D 0.8165	
A	0.806	38	0.803	43	0.806	47	0.8095	42
B	0.8115	42	0.8105	30	0.811	48	0.8135	40
C	0.814	70	0.815	100	0.815	98	0.8145	77
	0.8175	25						
D	0.8185	125	0.8185	175	0.8188	150	0.8188	150
EF	0.821	300	0.820	290	0.8208	300	0.821	295
		700		638		643		604

Table III. (Continued).

	(56)* D 0.8165		(57)* D 0.817		(58)* D 0.818		(59) D 0.8187	
A	0.806	45	0.8075	40	0.808	45	0.811	40
B	0.810	45	0.8115	40	0.8135	45	0.812	45
C	0.8145	95	0.815	100	0.817	105	0.814	92
D	0.8185	160	0.818	130	0.820	150	0.819	150
EF	0.821	295	0.821	330	0.822	300	0.823	305
		640		640		645		623

	(60)* D 0.8205		(61)E 0.814		(62)* E 0.8163		(63)* E 0.817	
A	0.8045	45	0.8075	33	0.8155	42	0.804	45
B	0.813	45	0.810	35	0.808	50	0.8075	50
C	0.8175	90	0.8125	80	0.8095	70	0.8145	102
					0.812	25		
D	0.822	170	0.818	125	0.8175	105	0.8205	150
					0.8182	32		
EF	0.823	270	0.8245	300	0.823	250	0.8245	300
	Unused, 70			—	0.8255	41		—
		692		573		615		647

	(64)* E 0.817		(65)* E 0.818		(66)* E 0.818		(67) E 0.818	
A	0.805	42	0.8065	90	0.805	38	0.805	40
			0.809	20				
B	0.810	42	0.810	110	0.811	38	0.811	45
C	0.8145	75	0.8155	186	0.8135	104	0.8145	85
			0.817	50				
D	0.820	135	0.8205	385	0.819	175	0.8185	125
			0.8205	75				
EF	0.8255	235	0.8255	650	0.8235	240	0.824	325
		529	0.8255	260		695		620
				1826				

3 tubes.

	(68)* E 0.8185		(69) E 0.819		(70) E 0.819		(71)* E 0.819	
A	0.8205	15	0.804	24	0.8115	21	0.8095	23
B	0.8043	35	0.808	40	0.814	31	0.8085	34
C	0.810	60	0.8145	85	0.815	90	0.814	80
	0.812	30						
D	0.817	160	0.8195	140	0.8165	120	0.820	160
EF	0.8225	300	0.824	300	0.824	330	0.824	280
		590		589		592		577

Table III. (Continued).

	(72)* E 0.8195		(73)* E 0.8195		(74) E 0.8195		(75) E 0.8197	
A	0.8145	30	0.8055	34	0.816	40	0.8025	40
B	0.8105	42	0.811	45	0.8135	42	0.8105	38
C	0.8135	103	0.8155	80	0.809	65	0.816	90
					0.814	34		
D	0.8195	160	0.820	120	0.8185	160	0.822	150
EF	0.824	285	0.824	290	0.824	260	0.8255	300
					0.827	30		
		620		569		631		618

	(76)* E 0.820		(77)* E 0.8205		(78) E 0.8215		(79)* E 0.822	
A	0.8045	48	0.806	32	0.8045	28	0.8105	32
B	0.812	40	0.8125	45	0.8135	36	0.8145	42
C	0.817	91	0.8175	90	0.8185	78	0.819	77
D	0.822	155	0.823	100	0.823	150	0.8225	155
EF	0.826	260	0.8245	330	0.8275	300	0.827	280
		594		597		592		586

	(80) E 0.822		(81) E 0.822		(82) E 0.824		(83)* A–B 0.804	
A	0.817	30	0.8083	26	0.8125	48	0.803	32
B	0.810	40	0.814	40	0.8127	48	0.8035	25
C	0.8153	46	0.8185	92	0.818	53	0.8035	63
	0.8163	42			0.819	50		
D	0.8225	160	0.824	140	0.8245	175	0.804	140
EF	0.8265	295	0.8265	270	0.828	200	0.806	275
					0.830	90		
		613		568	left,	50		535
						714		

	(84)* A–B 0.8065		(85)* A–B 0.808		(86)* B-C-D 0.8125		(87)* B-C-D 0.8125	
A	0.8035	40	0.8085	30	0.805	32	0.805	80
B	0.8055	40	0.807	30	0.808	42	0.8085	73
C	0.809	80	0.8065	92	0.813	85	0.812	118
							0.813	75
D	0.8085	155	0.8085	115	0.815	175	0.815	285
EF	0.811	300	0.8115	330	0.820	280	0.8175	520
		615		597		614		1151

2 tubes.

Table III. (Continued).

	(88)* C–D–E 0.813		(89)* C–D–E 0.813		(90)* B–C–D 0.8145		(91)* D–E 0.815	
A	0.8035	40	0.8035	130	0.8065	130	0.801	165
			0.807	20	0.808	27	0.8025	176
B	0.808	40	0.8077	160	0.809	137	0.8075	206
					0.8115	20	0.8085	156
C	0.8115	73	0.8125	330	0.813	305	0.812	330
	0.813	30	0.813	60	0.815	40	0.812	512
D	0.8155	160	0.815	550	0.815	560	0.817	340
			0.8175	90	0.8175	75	0.817	800
							0.817	150
EF	0.8195	290	0.8175	830	0.8175	775	0.8215	
		——	0.818	425	0.818	410	etc.	2733
		633		——		——		——
				2595		2479		5568
				4 tubes.		4 tubes.		9 tubes.

	(92*)*D–E 0.8163		(93) F 0.822		(94) F 0.822	
A	0.805	84	0.8107	35	0.804	28
	0.8075	20				
B	0.807	100	0.810	43	0.808	37
	0.8115	20				
C	0.815	205	0.814	70	0.8165	63
	0.816	45	0.816	25	0.817	30
D	0.820	350	0.8215	156	0.8218	146
	0.820	102				
EF	0.8225	500	0.8285	250	0.831	255
	0.8225	480	0.831	60		——
		——		——		559
		1906		639		

To chill and filter these products of two fractionations would have entailed too much loss. As it was, much uniting of samples which differed but slightly from one another was necessary to obtain sufficient oil for further fractionation. The unions which were made are given in Table IV.

Table IV.—*Products of Two Fractionations United for the Third Fractionation.*

Lot	Sp. gr.	Grade	Sp. gr.	cc.	Grade	Sp. gr.	cc.	Grade	Sp. gr.	cc.	Grade	Sp. gr.	cc.
						Fractions united							
95	0.805	B	0.8033	48	A	0.8035	240	B	0.8035	25			
		C	0.8035	63	A	0.804	65	D	0.804	140			
		A	0.8045	150	A	0.805	360	B	0.805	95			
		C	0.805	115									
96	0.807	A	0.8058	40	A	0.806	235	EF	0.806	275			
		A	0.8065	240	B	0.8065	100	D	0.8063	180			
					C	0.807	75	C	0.8065	92			
					C	0.808	80	A	0.8083	26			
97	0.8085	B	0.807	53	A	0.8075	290	A	0.8085	118			
		A	0.808	767									
98	0.8085	A	0.8072	20				B	0.8075	480	D	0.8075	270
		A	0.8077	38									
99	0.8105	A	0.8105	70	C	0.8105	270	A	0.811	40	B	0.811	580
		C	0.811	115									
100	0.8115	EF	0.811	300	A	0.8115	21	B	0.8115	308	C	0.8115	73
					EF	0.8115	920						
101	0.8125	C	0.8123	520	D	0.8125	160	EF	0.8125	820			
					B	0.813	45	C	0.8132	60			
102	0.813	No uniting necessary.											
103	0.8135	B	0.8125	180	C	0.8135	925						
		B	0.8135	106	EF	0.8135	715						
		B	0.8135	370									
104	0.814	No uniting necessary.											
105	0.814	C	0.814	500	C	0.8145	910						
106	0.8145	No uniting necessary.											
107	0.815	"											
108	0.8155	"											
109	0.8163	"											

Table IV. (Continued).

No.										
110	0.817	D	No uniting necessary.							
111	0.817	EF	"							
112	0.8175	C	0.8165 258		D	0.817	425	D	0.8172	75
		C	0.8175 200							
113	0.8175	EF	No uniting necessary.							
114	0.8187	EF	"							
115	0.819	D	0.8175 305		D	0.818	990			
116	0.819	EF	0.8185 845		EF	0.819	683			
117	0.819	D	No uniting necessary.							
118	0.819	EF	"							
119	0.8195	EF	"							
120	0.820	D	0.8195 475		D	0.820	600			
121	0.821	EF	No uniting necessary.							
122	0.8215	EF	"							
123	0.822	EF	0.8215 700		D	0.8218	460	EF	0.822	300
124	0.8225	EF	No uniting necessary.							
125	0.8235	EF	"							
126	0.824	D	0.823 250		EF	0.8235	860	D	0.824	140
127	0.8255	EF	No uniting necessary.							

Nine hundred and fifty cc. of each of these were fractionated by earth again, with the results given in Table V.

Table V.—The Third Fractionation.

	(95) A–D 0.805		(96) A–EF 0.807		(97) A–C 0.8085		(98) A–D 0.8085	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8065	33	0.8045	37	0.806	40	0.8047	38
B	0.805	33	0.806	38	0.8068	40	0.8052	38
C	0.804	62	0.8065	65	0.807	58	0.808	70
	0.805	40	0.8083	25	0.8095	18	0.8093	30
D	0.8055	150	0.808	142	0.8093	154	0.8095	132
EF	0.808	315	0.8095	250	0.812	295	0.811	335
		633		557		605		643

	(99) A–C 0.8105		(100) EF 0.8115		(101) C–EF 0.8125		(102) C 0.813	
A	0.8105	33	0.8065	30	0.808	33	0.806	26
B	0.810	36	0.809	36	0.8085	34	0.8105	33
C	0.8075	71	0.810	60	0.811	54	0.8105	50
	0.8085	17	0.812	20	0.8145	22	0.813	17
D	0.811	115	0.812	136	0.8145	162	0.813	136
EF	0.814	300	0.815	315	0.817	295	0.8157	365
		572		597		600		627

	(103) B–C 0.8135		(104) D–EF 0.814		(105) C 0.814		(106) C–D 0.8145	
A	0.8065	28	0.8042	35	0.804	40	0.803	33
B	0.810	33	0.8115	36	0.810	40	0.810	40
C	0.8135	60	0.8125	60	0.8142	58	0.8145	54
	0.8165	18	0.8147	28	0.816	25	0.816	22
D	0.815	150	0.815	175	0.8163	270	0.816	150
EF	0.817	325	0.819	230	0.8185	280	0.8185	260
		614		564		713		559

Table V. *(Continued)*.

	(107) D 0.815		(108) EF 0.8155		(109) D 0.8163		(110) D 0.817	
A	0.8035	45	0.809	52	0.810	33	0.8065	35
B	0.8115	47	0.811	47	0.8105	45	0.8125	40
C	0.815	85	0.815	55	0.8132	55	0.817	68
	0.8177	30	0.815	40	0.8145	33	0.818	30
D	0.8175	156	0.8165	170	0.8185	140	0.8195	145
EF	0.8195	300	0.8185	255	0.8215	275	0.821	290
		663		619		581		608

	(111) EF 0.817		(112) C–D 0.8175		(113) EF 0.8175		(114) EF 0.8187	
A	0.8043	30	0.8145	35	0.8065	35	0.817	30
B	0.8105	32	0.811	32	0.812	48	0.8065	25
C	0.8152	65	0.8165	60	0.8155	75	0.8122	30
	0.816	43	0.818	30	0.8175	18	0.813	15
D	0.8182	160	0.819	150	0.8185	150	0.8175	150
EF	0.8205	290	0.822	245	0.8225	283	0.822	340
		620		552		609		590

	(115) D 0.819		(116) EF 0.819		(117) D 0.819		(118) EF 0.819	
A	0.8055	16	0.8032	30	0.8045	33	0.805	30
B	0.807	lost	0.8115	36	0.813	38	0.813	30
C	0.816	43	0.816	52	0.8175	60	0.8165	60
	0.817	30	0.820	21	0.8175	34		10
D	0.820	130	0.8205	160	0.8215	150	0.821	154
EF	0.8225	300	0.8235	240	0.8235	325	0.8243	295
		lost		539		640		579

Table V. (Continued).

	(119) EF 0.8195		(120) D 0.820		(121) EF 0.821		(122) EF 0.8215	
A	0.805	23	0.805	33	0.8075	33	0.803	41
B	0.814	35	0.811	35	0.814	41	0.811	43
C	0.8165	58	0.817	53	0.8182	63	0.8165	60
	0.8175	32	0.8175	35	0.819	18	0.818	23
D	0.8205	152	0.822	165	0.822	150	0.8225	182
EF	0.823	300	0.825	310	0.8245	273	0.828	270
		600		633		578		629

	(123) D–EF 0.822		(124) EF 0.8225		(125) EF 0.8235		(126) D–EF 0.824	
A	0.808	34	0.807	31	0.804	35	0.805	35
B	0.813	35	0.8095	27	0.813	40	0.814	35
C	0.8178	52	0.8175	65	0.8185	70	0.820	60
	0.8192	42	0.8185	17	0.8195	21	0.821	20
D	0.8233	155	0.8232	150	0.8252	144	0.8253	170
EF	0.8265	260	0.8275	300	0.829	280	0.828	300
		578		590		590		620

	(127) EF 0.8255	
A	0.8055	45
B	0.8155	40
C	0.821	75
	0.823	25
D	0.8275	170
EF	0.830	280
		635

From the products of the third fractionation, oil of five grades was obtained in sufficient quantity by uniting fractions as given in Table VI., the results of the fourth fractionation being given in Table VII.

Table VI.—Products of Three Fractionations United for the Fourth Fractionation.

Lot.	Sp. gr.	Composed of				Composed of			
128	0.815	(99)	EF	0.814	300 cc.	(100)	EF	0.815	315 cc.
		(101)	C	0.8145	22 "	(101)	D	0.8145	162 "
		(103)	D	0.815	150 "	(104)	C	0.8147	28 "
		(104)	D	0.815	175 "	(105)	C	0.8142	58 "
		(106)	C	0.8145	54 "	(107)	C	0.815	85 "
		(108)	C	0.815	55 "	(108)	C	0.815	40 "
		(109)	C	0.8145	33 "	(111)	C	0.8152	65 "
									1542
129	0.8168	(101)	EF	0.817	295 cc.	(105)	D	0.8163	270 cc.
		(102)	EF	0.8157	365 "	(106)	D	0.816	150 "
		(103)	EF	0.817	325 "	(108)	D	0.8165	170 "
									1575
130	0.819	(104)	EF	0.819	230 cc.	(108)	EF	0.8185	255 cc.
		(105)	EF	0.8185	280 "	(113)	D	0.8185	150 "
		(106)	EF	0.8185	260 "	(109)	D	0.8185	140 "
									1467
131	0.8205	(107)	EF	0.8195	300 cc.	(115)	D	0.820	130 cc.
		(110)	D	0.8195	145 "	(116)	D	0.8205	160 "
		(111)	EF	0.8205	290 "	(118)	D	0.821	154 "
		(119)	EF	0.8205	152 "				1315
132	0.823	(113)	EF	0.8225	283 cc.	(120)	D	0.822	165 cc.
		(115)	EF	0.8225	300 "	(121)	D	0.822	150 "
		(119)	EF	0.823	300 "	(122)	D	0.8225	182 "
									1380

Table VII.—The Fourth Fractionation.

	(128) C–EF 0.815 Sp. gr.	cc.	(129) D–EF 0.8168 Sp. gr.	cc.	(130) D–EF 0.819 Sp. gr.	cc.	(131) D–EF 0.8205 Sp. gr.	cc.
A	0.8135	19	0.812	30	0.8115	24	0.8095	18
B	0.815	27	0.8122	42	0.8127	35	0.813	26
C	0.8118	50	0.8165	55	0.8173	60	0.819	45
	0.813	15	0.818	25	0.8185	22	0.8195	17
D	0.8147	140	0.818	160	0.820	160	0.8215	130
EF	0.8175	360	0.8195	305	0.8215	310	0.824	340
		611		617		611		576

	(132) D–EF 0.823	
A	0.8092	35
B	lost	35
C	0.8195	60
	0.8213	25
D	0.8235	150
EF	0.826	280
		585

To better compare the oils of different specific gravities which were obtained by the process just described five samples of 300 cc. each were separated, by distillation, into ten fractions. Each was distilled in the same 500 cc. distilling bulb, which was heated by an electric stove entirely surrounding the bulb. Each was first heated to 200° under atmospheric pressure and then to 360° under 50 mm. pressure. The diminished pressure was obtained by means of a large Chapman water pump and kept constant at 50 mm. by the use of a valve which automatically admitted air to the evacuated system whenever the pressure fell below 50 mm.

This valve was constructed from a piece of iron pipe one inch in diameter and five feet long. The lower end was closed with a cap and the pipe filled with mercury to a depth of 76 cm. The upper end of the pipe was closed with a two-hole rubber stopper. In one hole was a long glass tube,

with the lower end beveled, which reached to the bottom of the mercury and which could be raised or lowered as the barometer varied from day to day. In the other hole of the stopper was a tube which passed just through the stopper and which was connected on the outside with the apparatus to be exhausted. To prevent mercury from being drawn up and over into the apparatus by the air admitted, the end of the tube inside the stopper was drawn out and bent at a right angle and over this was slipped a cap made of larger tubing which was closed at the bottom but which had a fine opening in the side for air. This cap was about six cm. long and extended about three cm. below the end of the tube inside. If any mercury passed through this first fine opening into the cap, it would fall to the bottom without being drawn over into the apparatus or clogging the fine opening in the tube leading to it. With this valve there was no difficulty in keeping a pressure of 50 mm. constant to within one mm.

The specific gravity, viscosity, and percentage absorbed when treated with concentrated sulphuric acid (sp. gr. 1.84), of each distillate of sufficient volume, which was not too viscous or partly solid, was determined.

Viscosity was measured by taking the time of flow of a measured volume of oil through a capillary, the viscometer used being the one described by Ostwald and Luther and modified by Jones and Veazey.[1] The capacity of the small bulb was 4.5 cc. and the diameter of the capillary such as to require from five to eight minutes for that amount of oil to flow through it, and 1 minute 2.6 seconds for the same amount of water. The viscosity as well as specific gravity was always measured at 20°.

Viscosities have been calculated from the following formula: $\eta = \eta_0 \dfrac{TS}{T_0 S_0}$, in which η_0 is the coefficient of viscosity for water, S_0 is the specific gravity of water, and T_0 the time of flow of water through any given capillary at a given temperature; η is the viscosity coefficient of the solution investigated, S is its specific gravity as compared with water as

[1] Z. physik. Chem., **61**, 651.

unity at any given temperature, and T is the time of flow of the given solution at that temperature. The value for pure water at 20° was taken from the work of Thorpe and Rodger.[1]

Thirty cc. of each of these distillates, where that much oil was available, or the whole of the fraction when it was not equal to 30 cc., were mixed with an equal volume of concentrated sulphuric acid (sp. gr. 1.84) and shaken half an hour or longer in a shaking machine. The oil and acid were then poured into a separating funnel and the acid drawn off. The oil was then washed twice with water, once with aqueous sodium hydroxide, again with water, and then with this last wash water poured into a burette and allowed to settle. After standing overnight the volume was read.

The oils boiling below 200° (50 mm.) separated clear, but the heavy distillates were milky from water. The volume of these milky oils was read, their specific gravity determined, and then the milkiness was removed by shaking and heating to 60° or so with calcium chloride. The specific gravity of the clear oil was then measured and the proper correction applied to the volume of the milky oil. In no case, however, was this correction at all large, and only for the three or four heaviest oils did it exceed one-half of 1 per cent, the largest correction of all being 2.6 per cent for the distillate between 230°–260° of the oil of sp. gr. 0.824. An attempt to treat with acid the oils selected for distillation resulted in so much loss from the formation of emulsions that the loss in volume and change in specific gravity could not be determined with any degree of accuracy.

[1] Phil. Trans. [A], **185**, 397 (1894).

Table VIII.—Degree of Fractionation Obtained by Distillation.

		(1)	(2)	(3)	(4)	(5)	(6)
	Sp. gr.	0.801	0.808	0.815	0.8195	0.824	0.810
	Viscosity	0.0404	0.0555	0.0589		0.0657	0.0441
	Tubes passed through	1	3	3	4	4	crude oil
Normal pressure below 150°	cc.	36	1	13.	5	2	45.
	Sp. gr.	0.720		0.737			0.714
	Viscosity	0.0052		0.0059			0.0047
	Acid treatment { Per cent abs.	4.4		....			8.6
	ment { Sp. gr.	0.722		0.7365			0.712
150°–200°	cc.	47	61	52	60	60	43
	Sp. gr.	0.749	0.7465	0.756	0.757	0.759	0.759
	Viscosity	0.0075	0.0073	0.0075	0.0073	0.0072	0.0076
	Acid treatment { Per cent abs.	3.4	4.4	8.2	11.3	12.0	9.3
	ment { Sp. gr.	0.749	0.7469	0.750	0.749	0.750	0.752
50 mm. pressure below 140°	cc.	10	9	3	6	10	19
	Sp. gr.						0.7805
	Viscosity						0.0112
	Acid treatment { Per cent abs.						11.9
	ment { Sp. gr.						0.7735

Table VIII. (Continued).

		(1)	(2)	(3)	(4)	(5)	(6)
140°–200°	cc.	69	75	80	80	73	48
	Sp. gr.	0.790	0.790	0.797	0.800	0.8015	0.804
	Viscosity	0.0212	0.0185	0.0211	0.0216	0.0196	0.0254
	Acid treat- { Per cent abs.	3.4	4.4	8.9	9.6	14.8	11.0
	ment { Sp. gr.	0.790	0.7885	0.7915	0.795	0.7915	0.799
200°–230°	cc.	25	30	23	25	30	21
	Sp. gr.	0.813	0.8135	0.818	0.8225	0.822	0.823
	Viscosity	0.0556	0.0594	0.0573	0.0661	0.0505	0.0593
	Acid treat- { Per cent abs.		4.3	11.0	8.4	10.5	8.7
	ment { Sp. gr.	0.813	0.8125	0.816	0.8217	0.818	0.8175
230°–260°	cc.	23	27	23	20	24	22
	Sp. gr.	0.8255	0.826	0.830	0.833	0.838	0.8355
	Viscosity	0.1106	0.1150	0.1116	0.1168	0.1259	0.1248
	Acid treat- { Per cent abs.	3.4	8.5	7.0	8.8	7.6	12.6
	ment { Sp. gr.	0.8255	0.8255	0.828	0.832	0.833	0.830

Table VIII. (*Continued*).

260°–300° { cc	20	22	23	24	20	17
Sp. gr.	0.8395	0.838				
Viscosity	0.2520					
300°–340° { cc	25	30	27 solid	30 solid	26 solid	25 solid
Sp. gr.	0.847	0.849				
340°–360° cc	21 fluid	26 (below 355°) fluid	22 fluid		19 fluid	20 fluid
Residue cc	22 fluid	17 fluid	30 fluid	45 fluid	35 fluid	32 fluid
Total volume	298	298	296	295	299	292

By "fluid" in the above table is meant that the oil at 20° was partly solid but would flow when the bottle was inclined; by "solid," that the bottle could be turned upside down without the oil changing shape.

It was hoped that sulphuric acid of the strength used (sp. gr. 1.84) would dissolve only unsaturated hydrocarbons and leave untouched the paraffines and benzene. By long-continued shaking at ordinary temperature, however, benzene is dissolved by acid of this strength, provided that the acid is in large excess. One hundred cc. of benzene were completely dissolved in 434 cc. of acid on being shaken four hours.

Three of the distillates which had been shaken with acid, however, gave no action when treated with a mixture of equal parts concentrated sulphuric acid and fuming nitric acid, while distillates which had not been previously shaken with sulphuric acid were acted upon by this nitrating mixture. The action of the sulphuric acid, therefore, appears to have been complete.

The action of sulphuric acid shows that over 90 per cent of the oil dealt with consists of paraffine hydrocarbons, and that in the filtration through earth the paraffine hydrocarbons tend to collect at the top of the tube and the unsaturated hydrocarbons at the bottom.

The increasing amount dissolved by sulphuric acid in the heavier oils may be seen in the following curves. The abscissas represent temperatures and the ordinates volumes. The same distance upon the X axis is taken to represent a distillate, regardless of the number of degrees over which it may have been collected. The upper curve represents the percentage of the total volume which distilled between given temperatures; the lower curve, the percentage of the total volume recovered which was not absorbed by sulphuric acid (*i. e.*, the paraffine hydrocarbons). For the upper curve the ordinates were obtained by dividing the number of cubic centimeters in the distillate by the total volume of oil recovered. For the lower curve the ordinates were obtained by dividing the number of cubic centimeters in the distillate not absorbed by sulphuric acid by the total volume of oil recovered.

Temp. $0°$ $150°$ $200°$ $140°$ $200°$ $230°$ $260°$

Normal pressure.   50 mm. pressure.

Temp. 0° 150° 200°   140° 200° 230° 260°

Normal pressure.   50 mm. pressure.
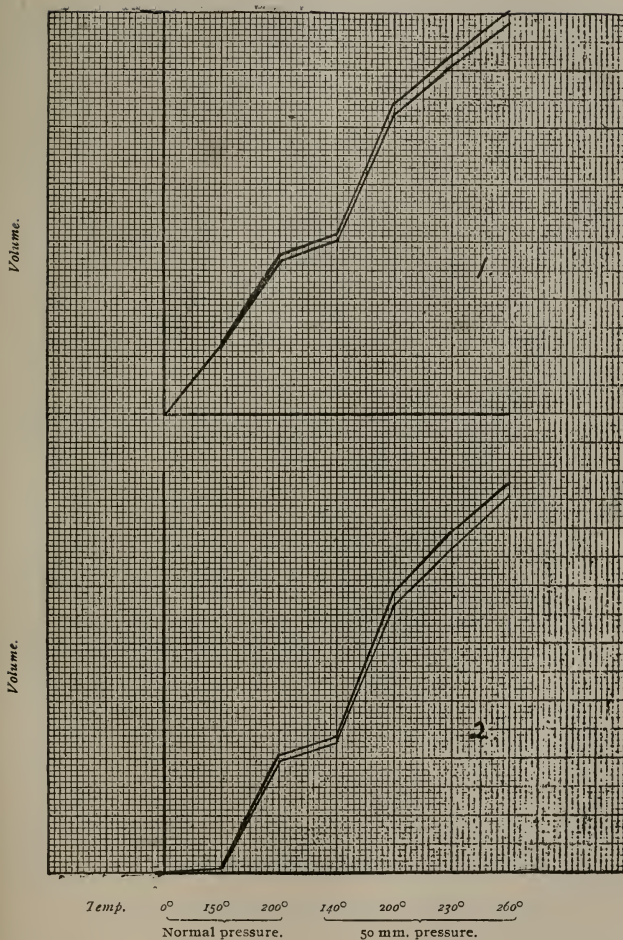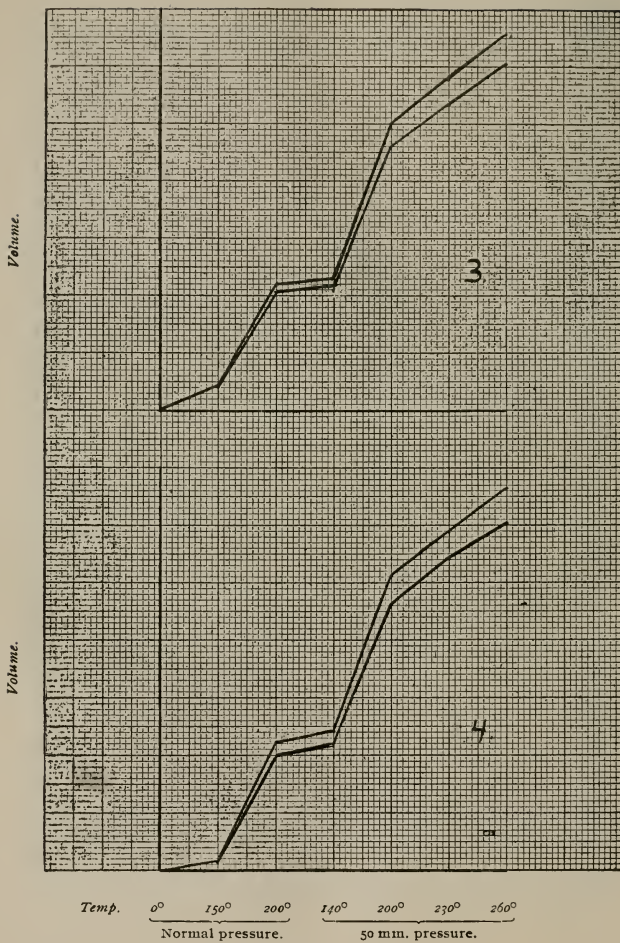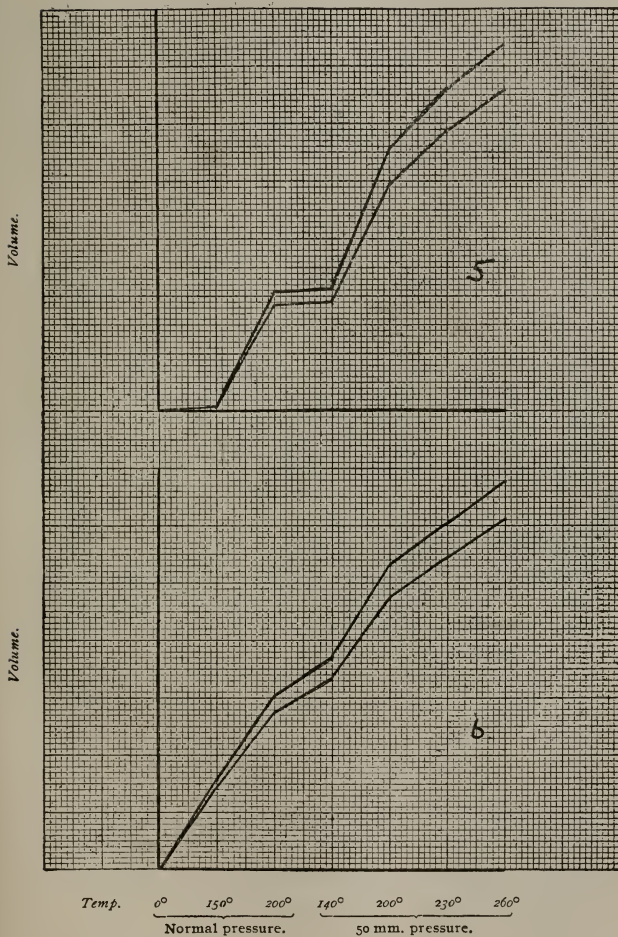
The area between the two curves represents the proportion of hydrocarbons soluble in sulphuric acid. This, it will be seen, is greatest for the oils of highest specific gravity.

On referring to Tables III. and V. it will be noticed that for several tubes the oil of grade A is heavier than that of grade B and sometimes of grade C. Tubes where this irregularity is marked are 48, 62, 68, 72, 74, and 80 of Table III., and 112 and 114 of Table V. A slight irregularity appears in 20, 21, 24, 27, 40, 71, and 85 of Table III. and in 99 of Table V. Where the oils in these cases are not colorless, the color is strongest in those whose specific gravity is greatest, so that although oil of the grade A has passed through the most earth it is yet more strongly colored than oil of grade B or C.

No reason for this variation has been established. It should be remembered, however, that the different oils rise in the earth with differing velocities, not because they differ from one another in specific gravity but because they differ in surface tension. A rough attempt was made to measure relative surface tensions by measuring the height to which different oils rise in the same capillary tube, but although a cathetometer was used and the level of the oil in the capillary brought to the same spot each time, the work sufficed only to show that the difference between the surface tension of the oils obtained was so slight as to require very careful measurement for the results to be of any value.

That viscosity shows the same irregularity as color and specific gravity in these oils appears from the the following measurements.

	(62)		(68)	
---	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.8155	0.0539	0.8205	0.0626
B	0.808	0.0469	0.8043	0.0469
C	0.8095	0.0509	0.810	0.0520
	0.812	0.0555	0.812	0.0554
D	0.8175	0.0525	0.817	0.0524
	0.8182	0.0535		
EF	0.823	0.0612	0.8225	0.0606

In (50) of Table III. an irregularity appears in grade B which is also found in the viscosity.

	(50) Sp. gr.	Vis.
A	0.8105	0.0532
B	0.8148	0.0559
C	0.810	0.0526
D	0.815	0.0526
EF	0.819	0.0552

The oils obtained by one fractionation of the crude petroleum have the following viscosities, the fractions measured being those previously given in Table I.

	(1) Sp. gr.	Vis.	(2) Sp. gr.	Vis.	(3) Sp. gr.	Vis.
A	0.796	0.0376	0.8012	0.0408	0.8022	0.0401
B	0.808	0.0529	0.804	0.0485	0.803	0.0470
C	0.8125	0.0501	0.807	0.0443	0.8075	0.0453
	0.8137	0.0529	0.809	0.0476	0.810	0.0471
D	0.815	0.0504	0.8125	0.0460	0.812	0.0472
E	0.818	0.0521	0.8185	0.0537	0.8175	0.0529
F	0.8205	..	0.823	..	0.821	..

That the viscosity does not increase with the specific gravity, particularly with the higher fractions, is apparent in two of the three series just given. The same is also shown in the following four samples taken from Table III.

	(21) Sp. gr.	Vis.		(22) Sp. gr.	Vis.
A	0.8038	0.0465		0.7997	0.0421
B	0.8035	0.0456		0.802	0.0485
C	0.8035	0.0456		0.8055	0.0502
	0.8052	0.0485			
D	0.805	0.0479		0.8063	0.0496
EF	0.807	0.0480		0.808	0.0510

	(47) Sp. gr.	Vis.		(53) Sp. gr.	Vis.
A	0.800	0.0453		0.803	0.0515
B	0.807	0.0538		0.8105	0.0563
C	0.814	0.0542		0.815	0.0684
D	0.816	0.0528		0.8185	0.0570
EF	0.819	0.0556		0.820	0.0559

This decrease of viscosity in the oils at the bottom of the tube appears to be a regular phenomenon in the dozen or so oils which have been tested. This point will be investigated further.

Water Fractionation.

To test the effectiveness of water fractionation alone, 1000 cc. of crude petroleum, previously chilled and filtered, of specific gravity 0.807, were mixed with 1000 grams of earth and allowed to stand 24 hours. Water was then added in small amounts and the oil collected.

	Sp. gr.	Volume of oil. cc.	Total water present. cc.
A	0.8148	44	500
B	0.8139	278	650
C	0.816	211	800
D	0.820	84	950
E	0.8225	28	1400
F	0.8245	28	2750
		673	

The fractions of large enough volume were then mixed with earth again and the oil replaced with water. One gram of earth was used for each cc. of oil, the earth first having been heated and allowed to cool.

B. 0.8139 278 cc. Stood 1.5 hours.			C. 0.816 211 cc. Stood 6 hours.			D. 0.820 84 cc. Stood 2.5 hours.		
Sp. gr.	Oil.	Water. cc.	Sp. gr.	Oil.	Water. cc.	Sp. gr.	Oil.	Water. cc.
0.8185	10	70	0.820	10	80	0.822	32	76
0.818	10	110	0.820	20	125	0.823	20	207
0.818	21	164	0.8195	72	250		—	
0.818	20	..	0.820	30	410		32	
0.817	42	..	0.820	10	588			
0.819	10	216		—				
0.820	44	277		142				
0.820	16	428						
0.8215	20	686						
	193							

It is apparent that while petroleum is fractionated by simply mixing the oil with fuller's earth and then displacing the oil from the earth with water, the fractionation is much less complete than when tubes are used, as previously described.

It will be noticed that although fractions C and D in the table last given are hardly separated at all by further treatment with earth and water, yet the specific gravity of all the oil recovered is higher than that of the oil used, *e. g.*, from C of sp. gr. 0.816 is obtained nothing lighter than 0.8195, and from D of sp. gr. 0.820 nothing lighter than 0.822.

To determine whether the specific gravity of the oil recovered will continue to rise after the oil is fractionated no further by repeated treatment, 330 cc. of sp. gr. 0.819, obtained by uniting several products of one fractionation of the crude petroleum, were mixed with 330 grams of earth and water was added.

	Sp. gr.	Vol. oil.	Total water present. cc.
A	..	6	64
B	0.8215	50	...
C	..	12	214
D	0.821	60	270
E	0.821	82	413
F	0.8225	26	613
		236	

Seventy-five cc. of E of sp. gr. 0.821 were next mixed with 75 grams of earth and 150 cc. of water were added. Fifty-one cc. of oil whose specific gravity was unchanged, but whose color was decreased, were obtained. Fifty cc. of this, when treated with earth and water, yielded 34 cc. of oil of considerably lighter color, but whose specific gravity was still 0.821.

Although only two-thirds of the oil used is recovered whenever oil is mixed with earth and then displaced with water, yet this loss does not seem to affect the specific gravity of the oil obtained for more than one or two treatments after the oil ceases to be fractionated. After this the oil recovered has the same specific gravity as the oil used.

The Oil Lost in the Earth.

The sum of the fractions of oil displaced from the earth is usually about two-thirds of the volume of the oil used.

A pressure of approximately 200 tons per square inch upon the earth from which water has displaced all the oil that it can results in the liberation of considerable water but very little oil. When earth which has been pressed is heated to 165° for three hours, considerable water distils over but much less oil than would be expected, *e. g.*, from 75 grams of earth which should contain 25 cc. of oil, but 4 cc. of oil were obtained. The earth was removed once from the flask and pulverized, and when the heat was discontinued the earth was thoroughly dry. On extraction with ether the earth gave a solution having the color of the original petroleum. The extraction was made with a Soxhlet extractor and continued until the extract was colorless. On evaporation of the ether there remained about 8 cc. of a heavy oil with the color of the natural petroleum. Pressure, heat, and extraction with ether together gave about half the amount of oil which the earth must have contained.

Earth which had been used once was allowed to dry for several weeks at room temperatures until it had lost all appearance of containing moisture. It was then pulverized, sifted, and used in a tube with the crude petroleum of sp. gr. 0.810 with the following results:

		cc.
8 cm. at top............	..	0
Next 8 cm.............	0.8284	10
Next 18 cm............	0.8225	45
Next 30 cm............	0.8143	60
	0.8155	80
Rest..................	0.8175	83
	0.819	114
		——
		392 cc.

Earth used, 720 grams.
Crude petroleum used, 740 cc.

The first oil up the tube evidently is absorbed by heavy material in the earth, while the first oil recovered dissolves

material from the earth, which increases its specific gravity beyond that of the next fraction.

To see how much of the weight of the earth just used was due to material which it had retained from its first use, 300 grams of earth were mixed with 300 cc. of crude petroleum and the oil displaced by water. The oil recovered measured 205 cc., and the weight of the earth after drying for several weeks at room temperature was 347.5 grams. Fully 15 per cent, therefore, of the weight of the earth used in the tube just mentioned was solid matter which it had retained from its first use.

In all cases the earth was heated before it was used because it was believed that heating decreased the amount of oil lost in the earth. The earth was heated usually in iron pans on a gas stove until it ceased to form geysers when stirred. A tube packed with earth which had not been heated gave the following results with crude petroleum of sp. gr. 0.810.

	Sp. gr.	Vol. cc.
Top 8 cm.............	0.803	30
Next 8 cm............	0.8045	38
Next 18 cm...........	0.8103	85
Rest.................	..	440
		593
Crude oil used.....................		930

Earth used, 948 grams.
Tube 5 feet long, $1^1/_4$ inches diameter.
20 hours required at diminished pressure.

In a case of water fractionation alone with unheated earth but 242 cc. of oil were recovered from 500 cc. of crude petroleum.

Results obtained toward the close of our work indicate that the loss of oil when unheated earth is used is much less than we had supposed it to be. The gain from heating the earth may not pay for the trouble of doing so, and this point should be investigated before any very extensive investigation is again undertaken.

Earth after heating must become thoroughly cold before it is used to pack tubes. The earth holds its heat for several

hours, and if it is used the same day upon which it is heated, there is apt to be contraction sufficient to allow the oil to run up the side of the tube as it would in a vacuum.

The length of the tubes used was five and one-half feet. A tube nine feet long was kept for two days with a constant diminished pressure of about 10 cm. mercury, and connected to the same vacuum pump with several five and one-half foot tubes. The oil was drawn to the top of the latter, which were removed and a second lot substituted. When these were likewise fully impregnated with oil the long tube was opened. The oil had ascended but 45 cm., showing that the diminished pressure had not penetrated that length of earth and reached the bottom of the tube.

A shorter tube in which the earth was packed very much harder, so that the tube filled with earth rang like an iron rod when pounded upon the floor, was connected with a vacuum pump at one end and a manometer at the other. Diminished pressure was indicated by the manometer when the column of earth was two feet long but not when it was two feet four inches.

The Fractionating Power of Substances Other than Fuller's Earth.

A clay from Topsham, Maine, was found which in tubes showed a power of fractionating as well as decolorizing the higher fractions. Compared with fuller's earth, the action was as follows.

	Sp. gr.	
	Clay.	Fuller's earth.
8 cm. at top..........	0.799	0.793
Next 8 cm...........	0.804	0.800
Next 8 cm...........	0.810	0.806
Next 10 cm..........	0.810	0.807
Next 30 cm..........	0.812	0.8092
Next 45 cm..........	0.812	0.8112
Time required,.......	69 hours.	76 hours.
Sp. gr petroleum used,	0.806.	

Tubes 5 feet long, $1^{1}/_{4}$ inches in diameter.

Neither powdered brick made from the same clay nor powdered feldspar showed any power of fractionation.

Another similar clay (from Mere Point, Brunswick, Maine) showed a power of water fractionation, but its behavior in a tube was not tested. Four hundred grams of this clay, previously sifted and heated, were mixed with 170 cc. of crude petroleum of sp. gr. 0.806 and allowed to stand 14 hours. Water was then added and the following fractions obtained:

Sp. gr.	Vol. in cc.	Total water present.
0.8165	24	104
0.817	60	133
0.8188	20	234
. .	6	374
	110	

The color was scarcely changed at all.

Summary.

(1) When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom.

(2) When water is added to fuller's earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterwards when more water is added.

(3) When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffine hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom.

(4) Whenever oil is mixed with fuller's earth and then displaced with water, about one-third of the oil remains in the earth.

This work will be continued in this laboratory, using a variety of oils and also studying a number of questions which have presented themselves.

JOHNS HOPKINS UNIVERSITY,
June, 1908.

CLXIII.—RESEARCHES ON PYRIMIDINES: SYNTHESES OF NEW DERIVATIVES OF 5-HYDROXY-URACIL (ISOBARBITURIC ACID).

[THIRTY-NINTH PAPER.]

By Treat B. Johnson and D. Breese Jones.

Johnson and Clapp[1] have shown that 1- and 3-alkyl derivatives of 2,6-dioxytetrahydropyrimidines, I., can be distinguished by the difference in their behavior towards diazobenzene-sulphonic acid. The 1-alkylpyrimidines, II., react with the sulphonic acid, in presence of alkali, giving red colored solutions, while the isomeric 3-alkylpyrimidines, III., do not give red colors under the same conditions. This interesting behavior of 1-alkylpyrimidines enabled Johnson and Derby[2] to determine the structures of the isomeric 1- and 3-benzyl derivatives of uracil and thymine.
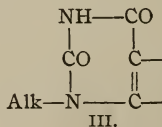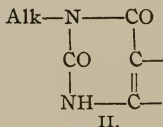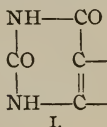
We have also found this diazo reagent to be of service for determining the structures of some new 1- and 3-alkyl derivatives of isobarbituric acid. The name—isobarbituric—signifies a compound isomeric with barbituric acid, IV., and having the constitution of a hexahydropyrimidine, as represented by formula V. The reactions of this pyrimidine, however, do not indicate a hexahydro compound but rather a tetrahydro-pyrimidine, as represented by formula VI., *viz.*, *5-hydroxyuracil.*
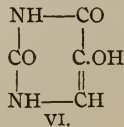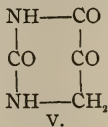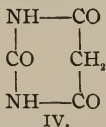
[1] J. Biol. Chem., **5**, 163 (1908).
[2] This Journal, **40**, 444 (1908).

Formula VI. is supported by the facts that the pyrimidine does not give an oxime[1] and also that the hydrogen of the 5-hydroxyl group is replaceable by the acetyl radical[2] when the pyrimidine is warmed with acetic anhydride. Furthermore, the pyrimidine and its ethyl ether[3] react with diazobenzenesulphonic acid, giving red colors as intense as that obtained with thymine.[4]

We shall describe in this paper the preparation and properties of 1-benzyl-5-hydroxyuracil (1-benzylisobarbituric acid), VII., 3-benzyl-5-hydroxyuracil (3-benzylisobarbituric acid), VIII., and also 1-benzylisodialuric acid, IX.

$$
\begin{array}{ccc}
\text{C}_6\text{H}_5\text{CH}_2\text{N}\!\!-\!\!\text{CO} & \text{NH}\!\!-\!\!\text{CO} & \text{C}_6\text{H}_5\text{CH}_2\text{N}\!\!-\!\!\text{CO} \\
\quad| \qquad | & \quad| \qquad | & \quad| \qquad | \\
\text{CO} \quad \text{COH} & \text{CO} \quad \text{COH} & \text{CO} \quad \text{COH} \\
\quad| \qquad \| & \quad| \qquad \| & \quad| \qquad \| \\
\text{NH}\!\!-\!\!\text{CH} & \text{C}_6\text{H}_5\text{CH}_2\text{N}\!\!-\!\!\text{CH} & \text{NH}\!\!-\!\!\text{COH} \\
\text{VII.} & \text{VIII.} & \text{IX.}
\end{array}
$$
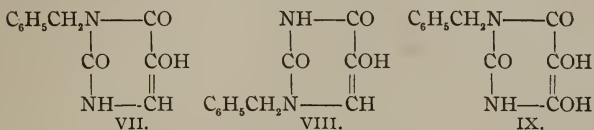
Johnson and McCollum[5] have shown that pseudoethylthiourea condenses smoothly with the sodium salt of ethyl α-ethoxy-β-oxyacrylate, giving 2-ethylmercapto-5-ethoxy-6-oxypyrimidine, X. This mercaptopyrimidine reacted with benzyl chloride, in presence of alkali, giving two isomeric pyrimidines, *viz.*, 1-benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine, XII., melting at 140°–141°, and 2-ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine, XIII., melting at 85°–86°. We did not observe the formation of 2-ethylmercapto-5-ethoxy-6-benzoxypyrimidine, XI. These two mercaptobenzylpyrimidines, XII. and XIII., were converted smoothly by hydrolysis with hydrochloric and hydrobromic acids into 1-benzyl-5-hydroxyuracil, XVII., melting at 230°, and 3-benzyl-5-hyroxyuracil, XIX., melting at 200°–210°, respectively. We also succeeded in isolating the two intermediate products of the hydrolysis, *viz.*, 1-benzyl-5-ethoxyuracil, XIV., melting at 150°, and 3-benzyl-5-ethoxyuracil, XVI., melting at 163°–164°.

[1] Behrend and Roosen: Ann. Chem. (Liebig), **251**, 240.
[2] Behrend and Roosen: *Loc. cit.*
[3] Johnson and McCollum: J. Biol. Chem., **1**, 437; THIS JOURNAL, **36**, 154.
[4] Johnson and Clapp: *Loc. cit.*
[5] *Loc. cit.*

XIII.

XVI.

XIX.

XI.

X.

XV.

XII.

XIV.

XVII.

XVIII.
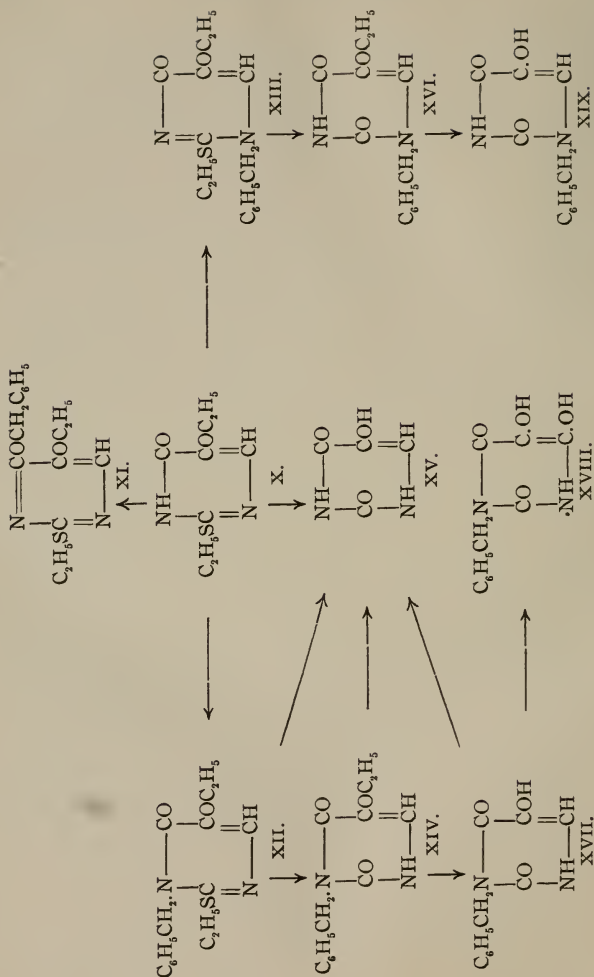
The structures of these pyrimidines were established in the following manner: The 1-benzyl-5-hydroxyuracil, XVII., melting at 230°, and the corresponding ethyl ether, XIV., reacted with diazobenzenesulphonic acid in presence of sodium hydroxide, giving beautiful red colors. The isomeric benzyl hydroxyuracil, XIX., melting at 200°–210°, and its ethyl ether, XVI., did not react with the sulphonic acid, with formation of red colors, indicating that these pyrimidines are 3-benzyl derivatives, as represented by the formulas above.

The benzyl-5-hydroxyuracils and their ethyl ethers are difficultly soluble in water. The hydroxyuracils are weak acids and stable in the presence of hydrochloric acid below 100°. 1-Benzyl-5-hydroxyuracil, XVII., was converted practically quantitatively into 5-hydroxyuracil (isobarbituric acid), XV., when heated with concentrated hydrochloric acid at 150°–160°.

1-Benzyl-5-hydroxyuracil, XVII., was converted quantitatively into 1-benzylisodialuric acid, XVIII., when it was suspended in cold water and then dissolved by adding a molecular proportion of bromine. The isodialuric acid crystallized from hot water without decomposition and gave a violet colored salt with barium hydroxide.

EXPERIMENTAL PART.

1-Benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine,

$C_6H_5CH_2N$——CO
C_2H_5SC COC_2H_5.—2-Ethylmercapto-5-ethoxy-6-oxy-
    N——CH
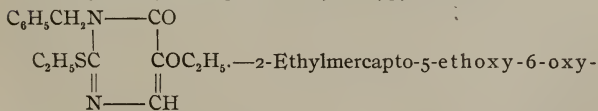
pyrimidine[1] (34 grams) and one molecular proportion of potassium hydroxide (9.0 grams) were dissolved in 250 cc. of boiling, absolute alcohol. Twenty-one and five-tenths grams of benzyl chloride were then added and the solution boiled until it gave no alkaline reaction when tested with moist turmeric (about 2 to 2.5 hours). The undissolved potassium chloride was then separated by filtration and the excess of

[1] Johnson and McCollum: *Loc. cit.*

alcohol removed by evaporation on the steam bath. We obtained a syrup which completely solidified after trituration with about 30 to 50 cc. of a 10 per cent solution of sodium hydroxide. When the alkaline solution was acidified with acetic acid we recovered 3.8 grams of the unaltered 2-ethyl-mercaptopyrimidine. The crude benzylpyrimidines were then extracted 3 times with boiling ether and the ether solutions saved (see 3-benzyl derivative below). The 1-benzylpyrimidine was insoluble in ether and melted without further purification at 134°–136° to an oil. It was purified for analysis by recrystallization from acetone or hot water. It separated in slender prisms melting at 140°–141° to an oil without effervescence. The compound is very soluble in alcohol, benzene, and acetone. It crystallizes from water in anhydrous condition. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{18}O_2N_2S$.	I.	Found. II.
N	9.65	9.81	9.80

2-Ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine,

$$\begin{array}{c} \text{N}\!-\!\!-\!\!\text{CO} \\ \| \quad\quad | \\ \text{C}_2\text{H}_5\text{SC} \quad \text{COC}_2\text{H}_5. \\ | \quad\quad \| \\ \text{C}_6\text{H}_5\text{CH}_2\text{N}\!-\!\!-\!\!\text{CH} \end{array}$$ —When the ether washings from the
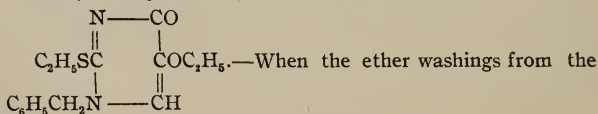
above experiment were heated on the steam bath to remove the ether we obtained a syrup which partially solidified after standing for 3 to 4 days. The crystalline material was separated from a small amount of oil by suction filtration and recrystallized from 95 per cent alcohol. It deposited, on cooling, in heavy, prismatic crystals which melted at 85°–86° to a clear oil with no effervescence. The pyrimidine is very soluble in acetone, alcohol, and ether, but insoluble in cold water. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{18}O_2N_2S$.	Found.
N	9.65	9.30

The total yields, and relative proportions of the crude isomeric benzylpyrimidines obtained in 4 experiments by alkyla-

tion of the mercaptopyrimidine, are given in the following table:

	Weight of 2-ethyl-mercaptopyrimidine taken. Grams.	Weight of crude 1-benzyl derivative obtained. Grams.	Weight of crude 3-benzyl derivative obtained. Grams.	Weight of unaltered 2-ethyl-mercaptopyrimidine recovered. Grams.	Percentage yield of 1- and 3-benzyl derivatives.
1	47.5	36.0 or 59.3%	24.7 or 40.7%	2.5	93.4
2	34.0	23.5 or 57.3%	17.5 or 42.7%	3.8	94.0
3	18.0	16.0 or 80.0%	4.0 or 20.0%	3.0	92.5
4	5.0	4.5	..	..	..

$$C_6H_5CH_2N\!\!-\!\!CO$$

1-Benzyl-5-ethoxyuracil, $\quad \overset{|}{CO} \quad \overset{|}{COC_2H_5}.$—This pyrimidine $\quad \overset{|}{NH}\!\!-\!\!CH$
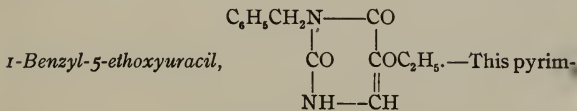
idine was always obtained mixed with 1-benzyl-5-hydroxy-uracil (see below) by hydrolysis of 1-benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine with concentrated hydrochloric acid. In one experiment, 5 grams of the mercaptopyrimidine were dissolved in 150 cc. of concentrated hydrochloric acid and the solution boiled for 12 hours. When the hydrochloric acid was removed, by heating on the steam bath, we obtained a mixture of the ethoxypyrimidine and benzylhydroxyuracil melting at 140°–180°. They were separated from each other by fractional crystallization from 95 per cent alcohol. This pyrimidine was more soluble in alcohol than the hydroxyuracil and crystallized in characteristic hexagonal prisms melting at 150° to an oil. This melting point was not raised by recrystallization from water. The pyrimidine did not contain water of crystallization and did not give a test for sulphur. When

it was dissolved in bromine water, and barium hydroxide added to the solution, a purple precipitate was obtained.

The pyrimidine reacted with diazobenzenesulphonic acid, in presence of sodium hydroxide, giving a brilliant, red colored[1] solution. The color slowly faded on standing. Analysis:

0.1160 gram of substance gave 11.8 cc. N at 19° and 759 mm.

	Calculated for $C_{13}H_{14}O_8N_2$.	Found.
N	11.38	11.6

1-Benzyl-5-hydroxyuracil (1-Benzylisobarbituric Acid),

$$C_6H_5CH_2.N\text{——}CO$$
$$CO \quad C.OH.$$
$$NH\text{——}CH$$
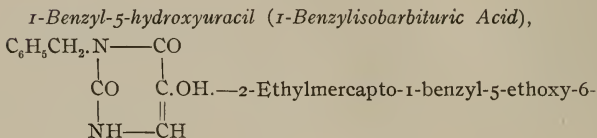
—2-Ethylmercapto-1-benzyl-5-ethoxy-6-oxypyrimidine is not converted quantitatively into this pyrimidine by boiling with hydrochloric acid. In order to obtain a complete hydrolysis within a few hours we found it necessary to proceed under the following conditions: 36 grams of the mercaptopyrimidine were dissolved in about 500 cc. of concentrated hydrochloric acid and the solution evaporated to dryness. We obtained a crystalline mixture of the intermediate ethoxypyrimidine (see above) and the benzylhydroxyuracil, which was then dissolved in 40 to 50 cc. of hydrobromic acid. After 3 to 4 hours' digestion with this acid the hydrolysis was complete. Too long digestion with hydrobromic acid is not advisable because the benzylhydroxyuracil slowly undergoes decomposition with formation of benzyl bromide and 5-hydroxyuracil. After removal of the hydrobromic acid the pyrimidine was purified by several recrystallizations from alcohol and water. The yield was good. The pyrimidine is less soluble in alcohol than the corresponding ethoxy derivative (see above). It crystallizes from alcohol in clusters of radiating prisms melting at 230° to an oil with effervescence. The pyrimidine separates from hot water in corpuscular crystals resembling in appearance the crystalline form of 5-hydroxyuracil (Analysis III.). A violet purple precipitate was obtained when the

[1] Johnson and Clapp: *Loc. cit.*

pyrimidine was dissolved in bromine water and barium hydroxide added to the solution. The pyrimidine reacts with diazobenzenesulphonic acid, in presence of sodium hydroxide, giving as intense a red color as 1-benzyl-5-ethoxyuracil. Analyses:

I. 0.0925 gram substance gave 10.2 cc. N at 19° and 756 mm.

II. and III. Nitrogen by Kjeldahl method.

	Calculated for $C_{11}H_{10}O_3N_2$.	I.	Found. II.	III.
N	12.84	12.60	12.95	13.0

5-Hydroxyuracil (Isobarbituric Acid) from 1-Benzyl-2-ethyl-mercapto-5-ethoxy-6-oxypyrimidine.—About 3.5 grams of the mercaptopyrimidine were dissolved in 50 cc. of concentrated hydrochloric acid and the solution heated for 3 hours at 150°–160°. When the tube was opened there was no pressure, and oil floated on the surface of the solution. This was separated and identified as a mixture of ethyl mercaptan and benzylchloride. When the acid solution was evaporated to dryness, we obtained a colorless substance which was difficultly soluble in water. It crystallized from hot water in hard, corpuscular crystals, which decomposed without melting at about 300°. It did not contain sulphur and chlorine. When the compound was dissolved in bromine water and barium hydroxide added to the solution, a purple precipitate was obtained. A nitrogen determination agreed with the calculated value for 5-hydroxyuracil.[1]

0.1321 gram substance gave 25.4 cc. N at 22° and 750 mm.

	Calculated for $C_4H_4O_3N_2$.	Found.
N	21.87	21.48

3-Benzyl-5-ethoxyuracil,

$$
\begin{array}{c}
\text{NH}\!-\!\!-\!\text{CO} \\
|\qquad\quad| \\
\text{CO}\quad\ \text{COC}_2\text{H}_5. \\
|\qquad\quad\| \\
\text{C}_6\text{H}_5\text{CH}_2.\text{N}\!-\!\!-\!\text{CH}
\end{array}
$$
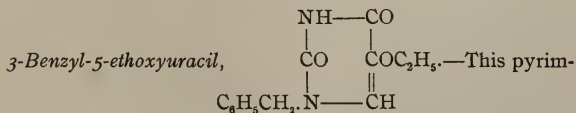
—This pyrimidine was formed smoothly when 2-ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine was digested with con-

[1] Behrend and Roosen: *Loc. cit.*

centrated hydrochloric acid. It appeared to be more stable, in presence of hydrochloric acid, than the isomeric 1-benzyl-pyrimidine. The compound is difficultly soluble in cold water but separates from a hot solution in needlelike prisms. It is very soluble in alcohol and separates from this solvent in the form of plates. It melts at 163°–164° to a clear oil. When the pyrimidine is dissolved in bromine water and barium hydroxide is added to the solution a violet precipitate is obtained. The pyrimidine did not react with diazobenzene-sulphonic acid to give a red colored solution. The solution assumed a yellow color which was permanent for 20 minutes.

Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}O_3N_2$.	I.	II.
		Found.	
N	11.38	11.23	11.40

3-Benzyl-5-hydroxyuracil (*3-Benzylisobarbituric Acid*),

$$\begin{array}{c} NH—CO \\ | \quad\quad | \\ CO \quad COH. \\ | \quad\quad || \\ C_6H_5CH_2.N——CH \end{array}$$—This compound was obtained when
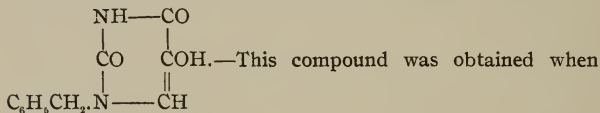
2-ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine was digested for several hours with hydrobromic acid. The pyrimidine crystallized from acetic acid in irregular crystals which melted from 200° to 210° according to the rate of heating. It was difficultly soluble in water and alcohol.

Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}O_3N_2$.	Found.
N	12.84	12.63

1-Benzylisodialuric Acid,

$$\begin{array}{c} C_6H_5CH_2N——CO \\ | \quad\quad | \\ CO \quad COH. \\ | \quad\quad || \\ NH——COH \end{array}$$—Five and
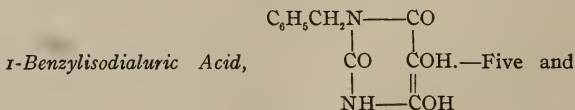
eight-tenths grams of finely pulverized 1-benzyl-5-hydroxyur-acil were suspended in 50 cc. of ice water, and 4.5 grams of bromine slowly added to the solution with constant stirring. The bromine immediately disappeared and the pyrimidine

completely dissolved. The excess of water was then removed by distillation under diminished pressure at a temperature of 50° to 70°. The isodialuric acid finally separated from the warm, saturated solution in beautiful, prismatic crystals. The solution was then cooled and the crystals separated by filtration. The yield of crude material was 6.1 grams. The pyrimidine is very soluble in hot water and separates, on cooling, in lenticular crystals melting at 139° with effervescence. The pyrimidine dissolved in a solution of barium hydroxide with formation of a violet colored solution. When heated at 105° the pyrimidine slowly underwent decomposition.

Analysis:

0.0979 gram substance gave 10 cc. of N at 20° and 768 mm.

	Calculated for $C_{11}H_{10}O_4N_2$.	Found.
N	11.96	11.81

NEW HAVEN, CONN.,
June, 1908.

CLXIV.—RESEARCHES ON PYRIMIDINES: THE THIO DERIVATIVES OF URACIL AND THE PREPARATION OF URACIL IN QUANTITY.

[FORTIETH PAPER.]

BY HENRY L. WHEELER AND LEONARD M. LIDDLE.

The impression is given in several text-books that the preparation of uracil, thymine, and cytosine by our synthetic methods[1] is no easier than the isolation of these substances from nucleic acids. Our syntheses are even given in Beilstein[2] as a process of formation (*Bildung*) and not as the best method of preparation (*Darstellung*). This view of our work is far from correct. In the past few years we have prepared a number of kilograms of these pyrimidines by our methods. The preparation of this amount of these substances from the nucleic acids would be a task for a factory.

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[1] Wheeler, Merriam, and Johnson: THIS JOURNAL, **29**, 478 and 492 (1903).
[2] Ergänzungsbände, IV., 550, 551, 1162.

For the preparation of uracil the sodium salt of formylacetic ester, $NaOCH=CHCO_2C_2H_5$,[1] was condensed, in alkaline, aqueous solution, with a pseudothiourea, $H_2N—C(SC_2H_5)NH$. The condensation product, 2-ethylmercapto-6-oxypyrimidine, on boiling with hydrochloric acid, easily gave off mercaptan, and a quantitative yield of uracil was obtained.

In this paper we describe a method of preparing uracil that is an improvement even over our previous synthesis. It has been our experience that thiourea gives uniformly larger yields of pyrimidine derivative than ethylpseudothiourea[2] when condensed with the sodium salt of formyl acetic ester.

The condensation with thiourea takes place with the formation of 2-thiouracil, I.,[3] as follows:

$$
\begin{array}{c c c c}
\text{HNH} & \text{C}_2\text{H}_5\text{OCO} & \text{HN——CO} & \text{C}_2\text{H}_5\text{OH} \\
| & | & | \quad\quad | & \\
\text{SC} \;\; + & \text{CH} & = \;\; \text{SC} \quad \text{CH} \;\; + & \\
| & || & | \quad\quad || & \\
\text{HNH} & \text{NaOCH} & \text{HN——CH} & \text{NaOH} \\
& & \text{I.} &
\end{array}
$$
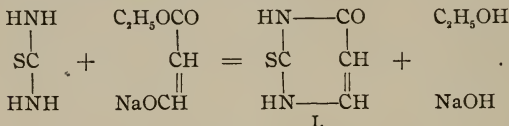
This condensation has the advantage over our previous method of avoiding the presence of mercaptan and since 2-thiouracil is more than ten times less soluble than 2-ethylmercapto-6-oxypyrimidine it separates more nearly completely on acidifying.

It remained then to discover a simple method of replacing the sulphur in this substance by oxygen. 2-Thiouracil, like other compounds of this class, is not desulphurized readily, if at all, by the ordinary methods. It forms more or less stable salts with the metallic oxides. List had a similar ex-

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[1] Wislicenus: Ber. d. chem. Ges., **20**, 2931 (1887).

[2] We have repeated our earlier attempts to condense the sodium salt of ethyl formylacetate with urea in aqueous solution, and thus obtain uracil directly, but without success. We have found that pyrimidine condensations which fail when water is used as the solvent may be brought about in alcoholic solution, in the presence of sodium ethylate. When the sodium salt of ethyl formylacetate, urea, and sodium ethylate were warmed for an hour on the steam bath and then tested for uracil with bromine water and barium hydroxide (J. Biol. Chem., **3**, 183 (1907)) no color was obtained. No precipitate was formed on acidifying the concentrated solution and no evidence of the formation of uracil was observed.

[3] Wheeler and Bristol: This Journal, **33**, 458 (1905).

perience with 2-thio-4-methyluracil.[1] To desulphurize this substance it was necessary to heat in a closed tube with hydrochloric acid for a few hours at 150°–160°. The thiohydantoins evidently also belong to this class.[2]

After a number of experiments we found that when 2-thiouracil was simply boiled with an aqueous solution of chloracetic acid, in slight excess, sulphur was easily removed, and on evaporation uracil remained. The yield was practically quantitative. The reaction probably involves the intermediate formation of the unstable 6-oxypyrimidine-2-thioglycollic acid, II., which, as we show below, on boiling with water gives uracil, III., and thioglycollic acid or its decomposition products, as follows:

$$
\begin{array}{ccc}
& \mathrm{HN\!-\!\!-\!\!CO} & \\
& | \qquad | & \\
\mathrm{HOCOCH_2SC} & \mathrm{CH} + \mathrm{H_2O} = \mathrm{OC} & \mathrm{CH} + \mathrm{HOCOCH_2SH.} \\
\| \qquad \| & \qquad | \qquad \| \\
\mathrm{N\!-\!\!-\!\!CH} & \mathrm{HN\!-\!\!-\!\!CH} \\
\mathrm{II.} & \mathrm{III.}
\end{array}
$$
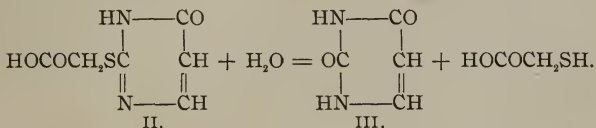
This reaction, which introduces nothing which can not be easily removed, is so smooth and satisfactory that we intend to investigate the use of chloracetic acid for desulphurization in other cases. At present, we have examined simply the new thio derivatives of uracil in this respect and have made the curious observation that while 2-thiouracil and 6-thiouracil, VII., are readily desulphurized, 2,6-dithiouracil, VIII., is not desulphurized on boiling with chloracetic acid but apparently forms the stable pyrimidine, 2,6-dithioglycollic acid, IX.

The preparation of the new thio derivatives of uracil was carried out as follows: 2-Ethylmercapto-6-chlorpyrimidine, V., from 2-ethylmercapto-6-oxypyrimidine,[3] IV., was treated with potassium hydrosulphide, giving 2-ethylmercapto-6-thiopyrimidine, VI.

When this compound was treated with concentrated hydrochloric acid on the steam bath mercaptan was evolved and

[1] Ann. Chem. (Liebig), **236**, 1 (1886).
[2] Bailey and Randolph: Ber. d. chem. Ges., **41**, 2495 (1908).
[3] Wheeler and Johnson: THIS JOURNAL, **29**, 496 (1903).

6-thiouracil, VII., was formed. On heating with dry hydrogen chloride, ethyl chloride was given off and 2,6-dithiouracil, VIII., was obtained. The latter was also prepared from 2,6-dichlorpyrimidine, X., and potassium hydrosulphide.

```
      HN——CO                    N══CCl                 HN——CS
      |    |                    |    |                  |    |
 C₂H₅SC   CH      →      C₂H₅SC   CH      →      C₂H₅SC   CH
      ‖    ‖                    ‖    ‖                  ‖    ‖
      N——CH                    N——CH                  N——CH
       IV.                      V.                      VI.
                                                 ↙        ↓
      N══CSCH₂CO₂H       HN——CS               HN——CS
      |     |             |    |               |    |
HCO₂CH₂SC   CH     ←     SC    CH             OC    CH
      ‖     ‖             |    ‖               |    ‖
      N——CH             HN——CH              HN——CH
       IX.               VIII.                VII.
                           ↑
                        N══CCl
                        |    |
                       ClC   CH
                        ‖    ‖
                        N——CH
                          X.
```

<div align="center">Experimental Part.</div>
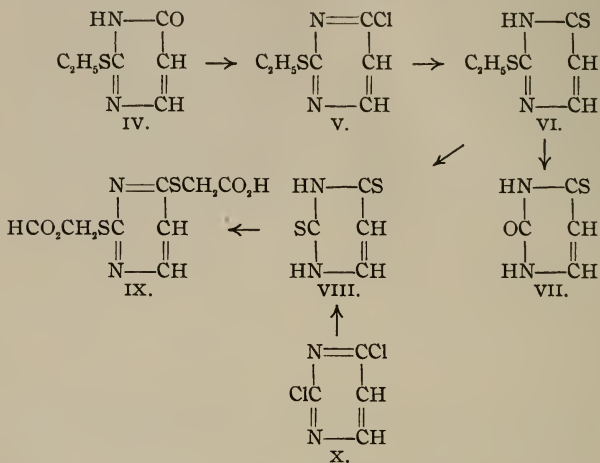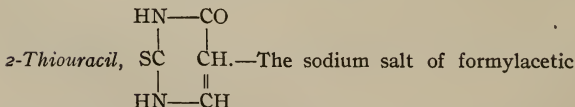
2-Thiouracil,
```
HN——CO
|    |
SC   CH.
|    ‖
HN——CH
```
—The sodium salt of formylacetic ester, prepared according to Wislicenus'[1] directions from 150 grams of ethyl formate, 150 grams of ethyl acetate, and 42 grams of sodium clippings in 500–600 cc. of dry ether, was dissolved in a cold, saturated, aqueous solution of 70 grams of thiourea. The solution was allowed to stand for an hour or so, then warmed on the steam bath, and finally cooled and acidified with acetic acid. Four such experiments gave about 280 grams of 2-thiouracil.

[1] Ber. d. chem. Ges., **20,** 2933 (1887).

A portion of this material was crystallized from water until it was obtained in colorless bunches of prismatic plates which melted with decomposition at about 340°. A solubility determination was then made as follows: The substance was placed in cold water and a rapid stream of air was drawn by suction, first through a wash bottle containing distilled water, and then through the solution containing the suspended substance. After two hours the undissolved material was filtered off and a weighed portion of the solution was evaporated to dryness and the residue was heated to constant weight at 110°.

To check the results a parallel series of determinations were made in which the substance was dissolved in hot water and the saturated solution was allowed to cool while air was drawn through for two hours as before. Solubility determinations were also made in this manner in the case of 2-ethylmercapto-6-oxypyrimidine and 2-methylmercapto-6-oxypyrimidine. It was found that 100 parts of water at 17° dissolved:

	Hot saturated solution.	Cold saturated solution.
2-Thiouracil	0.0533 gram	0.0598 gram
2-Methylmercapto-6-oxypyrimidine	0.6170 "	0.6620 "
2-Ethylmercapto-6-oxypyrimidine	0.8000 "	0.7930 "

The mercaptopyrimidines are therefore more than ten times as soluble in water as 2-thiouracil. 2-Thiouracil is almost insoluble in alcohol while the mercapto derivatives are very soluble. In our pyrimidine condensations alcohol is always present as a by-product, unless removed by evaporation; this reduces the yield in the case of the mercapto derivatives while in the case of thio derivatives just the opposite is true.

In accordance with its thioamide character, 2-thiouracil is a much stronger acid than uracil. It readily dissolves in sodium or potassium hydroxides and it forms very soluble, crystalline, anhydrous salts with these bases. It can be very conveniently crystallized from aqueous ammonia in which it is far more soluble than in water. It forms an ammonium salt which loses ammonia on drying or on boiling with water. Mercuric oxide removes 2-thiouracil from solution, forming an amorphous, anhydrous, insoluble salt.

The Copper Salt, $C_4H_2ON_2SCu.H_2O$.—Copper sulphate produces in aqueous solutions of 2-thiouracil, with or without alkali, an amorphous, mustard-yellow, insoluble precipitate. This salt can be boiled with water without alteration. It was dried in a desiccator over calcium chloride for analysis.

0.2997 gram substance lost 0.0276 gram on heating two hours at 105°–115°.

	Calculated for $C_4H_2ON_2SCu.H_2O$.	Found.
H_2O	8.67	9.20

0.1167 gram substance gave 0.045 gram CuO.

	Calculated for $C_4H_2ON_2SCu.H_2O$.	Found.
Cu	30.60	30.76

When silver nitrate is added to an aqueous solution of 2-thiouracil an amorphous, gelatinous, white precipitate is formed which does not blacken on boiling.
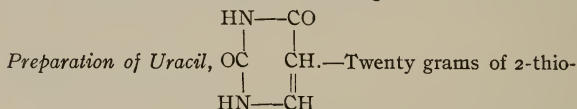
Preparation of Uracil,
$$\begin{array}{c} HN\text{---}CO \\ | \qquad | \\ OC \qquad CH \\ | \qquad || \\ HN\text{---}CH \end{array}$$
—Twenty grams of 2-thiouracil were boiled with one and a half molecular proportions of chloracetic acid in a large amount of water for one hour, then evaporated to dryness on the steam bath. The slightly colored residue was decolorized by means of animal charcoal, and on concentrating the solution 14.2 grams of pure white uracil, free from sulphur, were obtained. The yield in this case was 81 per cent of the calculated. More could have been obtained from the mother liquor.

In another experiment 30 grams of 2-thiouracil were boiled with 33 grams of chloracetic acid in about 700 cc. of water. When the material had dissolved the solution was allowed to evaporate to dryness on the steam bath. The residue was warmed with alcohol, filtered, and washed with alcohol. It was then free from sulphur and weighed 23.5 grams. This is 89.5 per cent of the calculated.

Uracil from 6-Thiouracil.—An aqueous solution of 2.1 grams of 6-thiouracil was mixed with 3 grams of chloracetic acid and

the solution was then evaporated to dryness on the steam bath. When the residue was crystallized from water 1.2 grams of pure uracil separated. This is 66 per cent of the calculated.

Ethyl 6-Oxypyrimidine-2-thioglycollate,

$$
\begin{array}{c}
\text{HN}\text{---}\text{CO} \\
| \quad\quad | \\
\text{C}_2\text{H}_5\text{CO}_2\text{CH}_2\text{SC} \quad \text{CH}.\tfrac{1}{2}\text{H}_2\text{O}. \\
\| \quad\quad \| \\
\text{N}\text{---}\text{CH}
\end{array}
$$

—Five grams of 2-thiouracil were
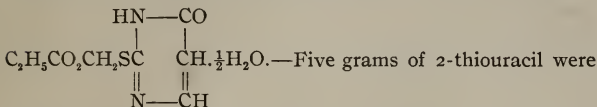
mixed with a solution of 0.9 gram of sodium in 30 cc. of alcohol and then 4.8 grams of ethyl chloracetate were added. The mixture was heated on the steam bath under a return condenser for one hour. The solution was then filtered and allowed to evaporate under reduced pressure in a desiccator. The crystalline residue after three recrystallizations from water yielded long, thin, glistening plates. These gave a strong test for sulphur and melted to a clear oil at 154°–155°. The substance was easily soluble in hot water and hot alcohol and nearly insoluble in cold water.

0.2852 gram substance lost 0.0138 gram when heated at 100°–115° for two hours.

	Calculated for $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_2\text{S}.\tfrac{1}{2}\text{H}_2\text{O}$.	I.	Found. II.	III.
H_2O	4.03	....	....	4.83
N	12.55	12.44	12.57	....

6-Oxypyrimidine-2-thioglycollic Acid,

$$
\begin{array}{c}
\text{HN}\text{---}\text{CO} \\
| \quad\quad | \\
\text{HOCOCH}_2\text{SC} \quad \text{CH}.\text{H}_2\text{O}. \\
\| \quad\quad \| \\
\text{N}\text{---}\text{CH}
\end{array}
$$

—This acid was obtained from the
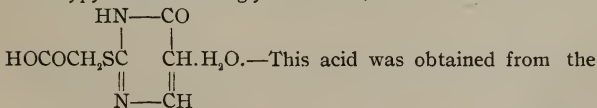
above ester by warming its aqueous solution with an excess of potassium hydroxide for a few minutes on the steam bath. The solution was then cooled and acidified with hydrochloric acid. A heavy, white precipitate formed which crystallized from water in bunches of fine prisms. This proved to be the hydrous form which separates slowly and melts at 178°. If the solution is stirred or the beaker scratched the anhydrous form generally results. The latter separates rapidly in loose

bunches of fine needles. The substance can be crystallized from alcohol. When it is boiled with water, thioglycollic acid separates and uracil is obtained.

0.2676 gram substance lost 0.0238 gram when heated two hours at $105°-110°$.

	Calculated for $C_6H_6O_3N_2S.H_2O$.	I.	Found. II.	III.
H_2O	8.82	8.89	. . . .	. . . .
N	13.72	. . . .	13.90	13.65

Some experiments were made with the object of preparing alkyl derivatives of 2-thiouracil. If a smooth alkylation on the sulphur would take place it would be the best method for the preparation of 2-alkylmercaptopyrimidines.

2-Ethylmercapto-6-oxypyrimidine.[1]—The action of sodium ethylate and ethyl iodide on 2-thiouracil in alcoholic solution gave 2-ethylmercapto-6-oxypyrimidine, melting at $152°$. When 30 grams or more of 2-thiouracil were employed the yields were much below the calculated. Unaltered 2-thiouracil was recovered when the substances were allowed to act in molecular proportions. It required repeated recrystallizations from alcohol to remove this impurity, so that the yields were unsatisfactory. If an excess of iodide and alkali were used the yield of 2-ethylmercapto-6-oxypyrimidine was still further reduced, owing to the formation of higher alkylated products. It was found that benzyl chloride acted more smoothly.

$$\text{2-}Benzylmercapto\text{-6-}oxypyrimidine, \quad C_6H_5CH_2SC \begin{array}{c} HN\text{——}CO \\ | \quad\quad | \\ \\ \| \quad\quad \| \\ N\text{——}CH \end{array} CH.\text{——Ten}$$
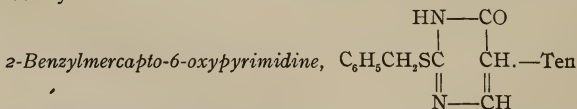
grams of 2-thiouracil and 4.4 grams of potassium hydroxide were dissolved in the smallest possible quantity of water on the steam bath and mixed with 9.9 grams of benzyl chloride. Alcohol was then added until the oil went into solution. The reaction took place immediately and gave long, slender, colorless prisms weighing 11.7 grams, or 68 per cent of the calculated.

[1] Wheeler and Merriam: This Journal, **29**, 478 (1903).

The same quantities of substances shaken repeatedly in a separatory funnel in aqueous solution without alcohol gave 12.4 grams, or 72 per cent of the calculated. The first method of preparation is smoother and is much easier, the product being more nearly pure.

The substance is soluble in about 16 parts of hot alcohol and in 50 parts of cold. In water or ether it is practically insoluble. Recrystallization from alcohol gave slender, twinned prisms which melted to a clear oil at 192°–193°.

	Calculated for $C_{11}H_{10}ON_2S$.	Found.
N	12.88	12.88

When the substance was warmed with hydrochloric acid on the steam bath, benzyl mercaptan separated. On evaporating and extracting with alcohol, uracil was obtained.

The Sodium Salt of 2-Benzylmercapto-6-oxypyrimidine, $C_{11}H_9ON_2SNa.3H_2O$.—The mercapto derivative was dissolved in an aqueous solution of sodium hydroxide and allowed to crystallize slowly in a desiccator. Large talclike plates formed which were very soluble in water and fairly soluble in alcohol.

0.3069 gram of substance lost 0.056 gram when heated at 100°–110° for two hours.

	Calculated for $C_{11}H_9ON_2SNa\ 3H_2O$.	I.	Found. II.	III.
H_2O	18.35	18.24	....	....
N	9.52	....	9.69	9.43

2-Ethylmercapto-6-thiopyrimidine,

$$\begin{array}{c} HN\!\!-\!\!CS \\ |\qquad | \\ C_2H_5SC\qquad CH. \\ \|\qquad \| \\ N\!\!-\!\!CH \end{array}$$

— E i g h t
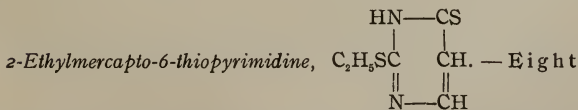
grams of 2-ethylmercapto-6-chlorpyrimidine[1] were treated with two and a half times the calculated quantity of potassium hydrosulphide in alcoholic solution. The solution was boiled for about 15 minutes and then evaporated to dryness on the steam bath and the residue taken up in a small quantity of

[1] Wheeler and Johnson: THIS JOURNAL, **29**, 496 (1903); **31**, 596 (1904).

water. The solution was shaken with ether, to remove any 6-ethoxy or unaltered chlor compound, and then made distinctly acid in the cold with acetic acid. A white flocculent precipitate separated, weighing 6.4 grams, or 80 per cent of the calculated. The substance was recrystallized twice from water, when it gave brilliant needlelike prisms, having a pale yellow color, which melted to a yellow oil at 149°. The material was easily soluble in alcohol and moderately in hot water. In cold water it was nearly insoluble. The properties of the compound were very similar to those of 2-ethylmercapto-6-oxypyrimidine, but a mixture of these substances melted at about 126°.

	Calculated for $C_6H_8N_2S_2$.	Found.
N	16.27	16.05

$$\text{6-Thiouracil,} \quad \begin{array}{c} \text{HN——CS} \\ |\qquad| \\ \text{OC}\qquad\text{CH.} \\ |\qquad|| \\ \text{HN——CH} \end{array}$$ —Two grams of 2-ethylmercapto-6-
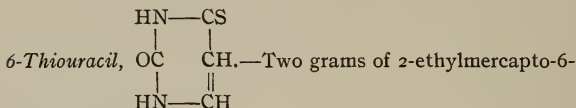
thiopyrimidine were evaporated to dryness on the steam bath with 10 cc. of concentrated hydrochloric acid. Mercaptan escaped. The residue was extracted with cold alcohol to remove unaltered ethylmercaptothiopyrimidine and the insoluble material was then found to weigh 0.8 gram, or 55 per cent of the calculated. In another experiment more prolonged action of acid gave a yield of 90.0 per cent; a small amount of uracil was also formed.

Like uracil and 2-thiouracil, 6-thiouracil is practically insoluble in strong alcohol but moderately soluble in hot water. It crystallized from hot water in small, light yellow needles. On rapidly heating it blackened above 270° and melted with effervescence at 328°. The properties of this substance are closely similar to those of 2,6-dithiouracil but a mixture of these compounds melted at 295°.

	Calculated for $C_4H_4ON_2S$.	Found.
N	21.87	21.66

$$
\begin{array}{c}
\text{HN}\!\!-\!\!\text{CS} \\
|\qquad| \\
\text{2,6-\textit{Dithiouracil}, SC}\qquad\text{CH} \\
|\qquad\| \\
\text{HN}\!\!-\!\!\text{CH}
\end{array}
$$
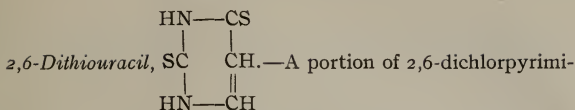
2,6-*Dithiouracil*, —A portion of 2,6-dichlorpyrimi-dine[1] was warmed on the steam bath with an aqueous solution containing somewhat more than four times the calculated quantity of potassium hydrosulphide. As soon as the oil disappeared, the hot solution was filtered from slight impurities and acidified with hydrochloric acid. This gave a yellow flocculent precipitate which was recrystallized from water. It was found to be difficultly soluble and it gave a feltlike mass of fine, bright yellow needles, which turned dark and decomposed above 230° without showing a definite melting point.

0.3215 gram substance gave 1.0278 gram $BaSO_4$.

	Calculated for $C_4H_4N_2S_2$.	I.	II.
			Found.
S	44.44	43.79	....
N	19.44	....	19.46

2,6-Dithiouracil was also obtained when 2-ethylmercapto-6-thiopyrimidine was melted in an oil bath at 170° and treated with dry hydrogen chloride. The material quickly solidified in the hot bath. It was then removed and crystallized from water, whereupon the characteristic yellow needles of 2,6-dithiouracil were obtained.

It was also found that when 2-ethylmercapto-6-oxypyrimidine was treated in the same manner 2-thiouracil was formed.[2]

Action of Chloracetic Acid on 2,6-Dithiouracil: *Pyrimidine-*

$$
\begin{array}{c}
\text{N}\!=\!\text{CSCH}_2\text{CO}_2\text{H} \\
|\qquad| \\
\text{2,6-\textit{dithioglycollic Acid}, HCO}_2\text{CH}_2\text{SC}\qquad\text{CH}\qquad\text{.—T w o} \\
\|\qquad\| \\
\text{N}\!\!-\!\!\text{CH}
\end{array}
$$
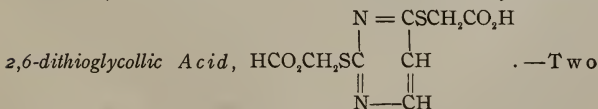
grams of 2,6-dithiouracil were dissolved in hot water and 5 grams of chloracetic acid were added. The solution was evaporated to dryness, the residue taken up in water and

[1] J. Biol. Chem., **3**, 287 (1907).

[2] See also Wheeler and Liddle: J. Am. Chem. Soc., **30**, 1157 (1908).

evaporated again, the operation being repeated several times or until the yellow color disappeared. The residue was then moderately soluble in alcohol and very difficultly soluble in hot water. It was crystallized from 600 cc. of boiling water, and 2 grams of white powder separated. Boiling with water or even warming with concentrated hydrochloric acid did not desulphurize this substance. When heated it decomposed above 200°.

	Calculated for $C_8H_5O_4N_2S_2$.	Found.
N	10.77	11.14

New Haven, Conn.,
September, 1908.

THE LIMITING CONDUCTIVITY AND DEGREE OF IONIZATION OF ALCOHOLIC SOLUTIONS.

By B. B. Turner.

The degree of ionization of alcoholic solutions cannot be determined with either the ease or the accuracy possible in the case of aqueous solutions, and in spite of numerous researches and the accumulation of a great quantity of data, there is still much uncertainty as to its value. The conductivity method suffers from two difficulties. Besides the doubt as to the validity of the usual assumption that the degree of ionization is given by the ratio of the molecular conductivity to the limiting value of the same function at infinite dilution, which probably does not hold with any great accuracy even for aqueous solutions at concentrations above half, or possibly one-tenth, normal, and may fail at still smaller concentrations in nonaqueous solutions, there is the great practical difficulty of determining the limit of the molecular conductivity, which is only reached at dilutions at which the actual conductivity is extremely small. The ebullioscopic method is free from these defects, but is only applicable to solutions of moderate concentration, and, owing to experimental difficulties, cannot give the same degree of accuracy as good electrical measurements.

The present investigation was undertaken at the suggestion of Prof. H. C. Jones, with the intention of relying chiefly upon the boiling point method as worked out and already applied by him to many alcoholic solutions. From such conductivity data as existed, it appeared probable that the molecular conductivity of solutions in ethyl alcohol would not become appreciably constant at a smaller dilution than about a million liters, and would therefore be incapable of experimental determination.[1] It has been found, however, that when necessary precautions are taken to reduce the conductivity of the solvent, and eliminate accidental fluctuations in the same during the course of each experiment, the molecular conductivity becomes appreciably constant at much more moderate dilutions. The boiling point method was tested and a great deal of time spent in various minor modifications, which, it was hoped, would increase its accuracy, but the results are not yet in a condition suitable for publication. The author hopes to be able to continue this work, and also to add to the conductivity data, but a change in circumstances makes it desirable to publish the results already obtained.

The ethyl alcohol used in this investigation was dried in the usual way by boiling with quicklime, in some cases after long standing over the same, for two or three days, and the degree of dehydration was in all cases controlled by determination of the specific gravity. As appeared in the course of the work, the conductivity alone is not a certain indication of freedom from water, as an alcohol was obtained with nearly 1 percent of water and a conductivity of only 0.183×10^{-6}

[1] The author has just become aware of a paper by Dutoit and Rappeport's (J. Chim. Phys., **6**, 545, Sept., 1908) in which the limiting conductivities of several salts in ethyl alcohol are determined by measurements at 18° at dilutions up to 4000-20000 liters. Needless to say he did not know of these measurements when the work described below was being carried out (Feb.-June, 1908). In the case of potassium iodide, Dutoit and Rappeport's results agree fairly closely with the present author's, as is shown by the following table in which the values are recalculated in reciprocal ohms, but the maximum of the molecular conductivity in the neighborhood of 20000 liters is not indicated.

V.	D. & R.	B. B. T.
500	36.4	36.9
1000	38.4	39.1
2000	39.6	41.0
4000	40.7	42.0
∞	41.9	42.85

mhos, which is 5 to 10 times lower than that of the "pure" alcohol used in many previous investigations; on the other hand, the most nearly absolute alcohol used usually had a higher conductivity than this until it had been redistilled several times from a clean flask through a tin-worm condenser. The best alcohol used was about 99.98 per cent and the average of that used for the accepted results about 99.9 per cent. It may not be amiss to recall here that Mendeléeff's tables of specific gravity in Landolt and Börnstein's "Tabellen," which are widely used for the calculation of the strength of aqueous alcohols, require a slight correction when the temperature of the determination has been read on a thermometer calibrated on the hydrogen scale, as the latter scale, which the certificates of the Phys. Tech. Reichsanstalt have made familiar, was not used by Mendeléeff. While the exact magnitude of this correction cannot be determined now, it is safe to assume that it amounts to about $0.15°$ C., corresponding to 0.03–0.04 per cent alcohol, which must be subtracted from the values for the percentage compositions given in the tables.[1]

The conductivity of the alcohol is naturally a question of great importance where high dilutions are to be made. Fortunately there is no difficulty in reducing this about 10 times below that of ordinary "conductivity" water, and exposure to air seems to affect it much less than it does water; probably because carbon dioxide forms no compound in alcohol as readily ionized as carbonic acid is in water. Alcohol having a conductivity as low as 0.3×10^{-6} mhos can be easily obtained, and in all but the preliminary experiments the conductivity of the alcohol used was below 0.2×10^{-6}, the average being about 0.15×10^{-6}, while in some cases it was as low as 0.080 to 0.075×10^{-6}.[2] To reduce exposure to the air as much as possible, the alcohol was at first stored in a bottle with a syphon of Jena glass, through which it was forced as needed by a rubber blowing-ball, but this precaution was found to be dispensible.

[1] See Andrews: J. Am. Chem. Soc., **30**, 359 (1908).
[2] These results agree almost exactly with those of Völlmer (Wied. Ann., **52**, 328 (1894)). The use of alcohol with considerably greater conductivity, approaching that of distilled water, seems hardly permissible.

The most important detail of practical manipulation proved to be the manner of making up solutions. To avoid frequent additions of solvent and withdrawals of solution, which give opportunity for absorption of water, as well as for accidental contamination with other electrolytes, and in order to insure greater accuracy in the dilutions, it was decided not to follow the Ostwald method of dilution in the cell, but to make up all solutions on a considerable scale in measuring flasks, from which the cell was filled after repeated rinsings. To insure accuracy, the cell was always refilled once more after making a measurement and the observation repeated; if the two differed appreciably, a third was taken. The necessity for this was found to depend on the past history of the cell.

Platinum electrodes in alcoholic solutions of salts seem to show a certain amount of absorption, such as has been described by Kohlrausch in the case of aqueous solutions of acids and bases, but not of salts. After a cell had been used for solutions of medium strength and thoroughly rinsed with a very dilute solution, a further slight decrease in conductivity was observable on refilling with the same, and sometimes constancy is not reached till the third or fourth observation. Allowing the solution to stand for 20 minutes to an hour in the cell before reading proved helpful, as though equilibrium were only attained by slow diffusion of the electrolyte out of the electrodes. A contrary but less noticeable tendency of the conductivity to increase when stronger solutions were used after weak ones was sometimes observed; evidently the residual diffusion of salt into the electrode was less in proportion to the total conductivity. I therefore made a habit of commencing a series of observations with the pure solvent, followed by the solutions in increasing order of strength. Platinized electrodes were naturally worse in this respect than bright ones, so that the latter were used wherever possible, and always in the best determinations at high dilutions and with the pure solvent.

The cells used were mostly of the well-known Arrhenius form as modified by Jones and Bingham,[1] with fixed electrodes fused into ground-glass stoppers. While this

[1] THIS JOURNAL, **34**, 493 (1905).

form has advantages in cleanliness and ease of manipulation, there is some danger of variation in the cell constant, due to the scraping of the electrodes against the sides of the cell in taking them out. With care in manipulation the error from this source is not appreciable when the distance between the plates is several millimeters, but as the influence of any slight distortion increases in inverse proportion to the distance between the plates, it is not advisable to make this less than about a millimeter. Even where the distance was about 5 mm. a change of nearly one-half per cent occurred during the course of the work, and was only detected on recalibration considerably later. In order to get a sufficiently high constant for the very pure solvent and for dilutions of 100,000 liters and over, I made a cell consisting of two platinum plates, 5 x 5 cm., rolled and welded in the form of cylinders, which were fixed concentrically by wires fused into tubes of Jena glass, and kept at a constant distance apart of about 1 mm. by means of drops of fusible glass. The glass tubes, which served as mercury cups to make electrical connection, were fastened in a cork which nearly closed the mouth of a Jena glass tube about 2 cm. in diameter and closed at the bottom. The constant of this cell being only 5.5, the resistance with the purest alcohol was about 35,000 to 70,000 ohms, which was low enough to be measured with sufficient accuracy. A great advantage in this form of cell is that the electrodes slide in and out smoothly, and having considerable stiffness owing to their cylindrical shape, any accidental contact with the sides of the cell has very little tendency to distort them. Stirring of the solution was effected by lifting and lowering the electrodes several times.

One very vital question in accurate work with alcoholic solutions has to do with the possible oxidation of the alcohol to acetic acid, during the experiments, by exposure to the air. That this did not play any serious part in this work is shown by the following experiment:

Three cells, with platinized electrodes, which had been allowed to stand a couple of days after using, the electrodes

remaining wetted with pure alcohol, were rinsed out with the same small quantity (about 42 grams) of a very pure alcohol whose conductivity had just been found to be 0.10×10^{-6} mhos and the rinsings were then returned to the measuring cell. The conductivity was now 0.37×10^{-6}, showing an increase of only 0.27×10^{-6} due to the whole amount of acetic acid washed out of the three cells. As the conditions for oxidation were so much more favorable than in the usual course of the measurements, when the electrodes were totally covered by the alcohol, and as the time was so much longer, it is reasonable to suppose that the gain in conductivity of a sample of alcohol during an experiment could hardly exceed one or two hundredths of a reciprocal megohm, and was probably less. The bright platinum of the cell used for the high dilutions would be much less likely to cause oxidation. If oxidation did occur in the course of the experiments it would show itself in a gain in conductivity on lifting out the electrodes to stir the liquid, and still more on allowing the cell to stand between two measurements. No evidence of a definite change could be noticed in the first case, but only the slight accidental changes due to differences in position of the electrodes, which it was the special object of these repetitions to test. Change on standing was more noticeable, but instead of a gain there was an almost uniform *loss* of conductivity, especially marked with the purest alcohols and most dilute solutions, if the alcohol had been recently distilled. A similar change in the conductivity of alcohol has been observed by Pfeiffer,[1] who attributes it to the solution of oxygen from the air. While there is nothing in my observations to exclude this view, it is difficult to see why a solution of oxygen in alcohol should act as an anti-electrolyte, or, in other words, why the oxygen should decrease either the number or the migration velocity of whatever ions may be present in pure alcohol. It seems to me more likely that the observed decrease in conductivity is the result of a chemical change, which may or may not be connected with the taking up of oxygen from the air,

[1] Pfeiffer: Wied. Ann., **26**, 31 and 226 (1885).

removing some trace of electrolytic impurity, perhaps an ethyl peroxide, in the fresh alcohol. This change seems to be accelerated by platinum, but the conductivity of the alcohol was observed to decrease even in the bottle, as is shown by the following observations:

A sample of alcohol of the sp. gr. o.78948 at 20°/4 gave a conductivity, when first tested, two or three days after distillation, of o.126 × 10^{-6} reciprocal ohms, which decreased to o.105 two days later. Another sample gave o.126 on April 30th and o.111 on May 1st. When allowed to stand in the cell in contact with bright platinum overnight, another alcohol decreased in conductivity from o.224 to o.189. The change becomes slower after a few days. Thus a sample giving o.224 on March 24th gave o.195 on April 16th, a loss of only o.03 in 23 days. As against this, there was frequently a gain in conductivity on standing overnight in the cell, due to solution of minute amounts of substance either from the glass or the platinum electrodes, and this was so much increased on heating that it was impossible to obtain concordant results for the temperature coefficient of the purest alcohols, as will be shown later.

The action of absolute alcohol on glass is much less than that of water. A sample kept for 26 days in an ordinary glass bottle, protected from the air by a drying tube, increased only o.1 × 10^{-6} mhos, and in Jena glass the gain was naturally less.

A much more marked effect was found in the behavior of alcohol of very low conductivity on bringing it into a new vessel which had been thoroughly cleaned and dried in the ordinary way, and in this was found the great cause of the earlier inconsistent results at high dilutions. The act of drying seems to loosen the surface of the glass, or else the solvent action is so much increased by the higher temperature that even in the short time in which the drops of water remain on the glass enough is acted on to greatly increase the conductivity of the alcohol which is afterwards put in the vessel. This source of error may be largely avoided by using only vessels which have been freed from water by *rins-*

ing with alcohol of the required purity, and never allowed to dry after washing. Thus an alcohol giving a conductivity 0.174×10^{-6}, when sampled from the stock bottle, gave 0.185, 0.181, 0.195, respectively, after pouring into three measuring flasks which had been rinsed, as above, but 0.356 and 0.410 in two others which had been equally carefully cleaned, then rinsed with ordinary distilled water, then three times with "conductivity" water of about 2×10^{-6}, and then dried by heating for a few minutes in a clean drying oven and blowing out the steam with a current of filtered air. From this experiment it was plain that discrepancies in previous work at dilutions of over 10,000 liters, at which the total conductivity is less than 5×10^{-6}, were due to an increase in the conductivity of the solvent between the time at which it was measured alone and its introduction as solution into the measuring cell. It was therefore made a uniform custom to test the conductivity of *each* quantity of alcohol used for a dilution *after* it had been poured into the measuring flask, just before making the solution; the cell itself having been thoroughly cleaned by rinsing with conductivity alcohol, assurance of which was obtained by taking its resistance in the process, there remains only the possibility that impurity may be introduced from the surface of the pipette. To test this, 10 cc. were drawn up into a clean pipette from the alcohol in the cell after its conductivity had been found to be 0.116×10^{-6}, and allowed to run back. The conductivity was then 0.122. As the pipette was used only to deliver solutions with a conductivity many times greater (usually 200 to 500×10^{-6}), this increase would be quite inappreciable. Even where the correction for the solvent amounted to a large fraction of the total conductivity, it was not thought necessary to apply any correction for such an increase, inasmuch as the much larger volume of alcohol in the measuring flask would reduce this correction to about 0.001 or 0.002. Care must be taken, however, not to use the *mouth* in pipetting, on account of the danger of introducing carbon dioxide. In all the later experiments the pipette was filled by the help of a suction pump.

Solutions up to about N/250 were made by direct weighing, and from these the higher dilutions were made by volume. In order to avoid the chance of error in repeated dilutions, flasks up to 250 cc. and a 2 cc. pipette were used when necessary, and to avoid the uncertainty as to the amount delivered, the flask, containing some alcohol, was weighed before and after running in the quantity from the pipette, from which the volume actually delivered could be ascertained to less than 0.01 cc. by means of an approximate value for the specific gravity.

All the concentrations are calculated on the basis of *volume normality* at 20°. In comparison with the results of the boiling point method it must not be forgotten that the latter are usually expressed as molecular concentrations *per gram* of alcohol, and therefore appear to be about 20 per cent higher. Conductivities are expressed in *reciprocal ohms*, not, as is still frequently done, in Siemen's units.

Measurements were made at several different temperatures and especially at as high temperatures as practicable, with the object of ascertaining the degree of ionization at the boiling point for comparison with the ebullioscopic method. It was found quite possible to make reasonably satisfactory measurements at 65° C., though many solutions were not measured above 50°. The better to obtain the change of the temperature coefficient with temperature, measurements were also made at 0° C. It was found, in fact, that while the conductivity-temperature curve for the stronger solutions is nearly a straight line, in the case of very dilute solutions it has a decided curvature, so that very incorrect results would be obtained for the limiting value of the molecular conductivity at 78° by linear extrapolation with a temperature coefficient obtained by measurements in the neighborhood of 25° C. As a check on the accuracy of the extrapolation, two solutions were finally measured at 78° in specially made cells of Jena glass which were sealed with the blowpipe and completely immersed in the bath, except for a side tube that served as a handle, in such a way as to avoid distillation of the cell contents from one part of the cell to another.

Slight indications of this trouble were sometimes noticed in the usual type of cell, but not enough to affect the results by more than one or two parts in a thousand. The bath used was jacketted with asbestos and covered with an asbestos lid, and could be kept constant to $0°.1$ by an Ostwald thermoregulator.

In working at $50°$ and $65°$ decided changes in conductivity, especially of the more dilute solutions, were noticed when the same solution was tested at $25°$ before and after heating. In some cases the conductivity increased, indicating concentration by evaporation or solution of impurities, but more often at high dilutions there was a decrease of conductivity, amounting sometimes to 2 per cent or more. This decrease seems to be due to a change in the conductivity of the alcohol itself, as its relative importance is roughly proportional to the dilution, the absolute amount of the change averaging about 0.1×10^{-6}. For this reason the molecular conductivity at the higher temperatures could not be calculated directly without correction. I have assumed that the change, if not complete at the higher temperature, at least comes to a standstill, within the limits of experimental error, on rapid cooling to $25°$, and I have therefore compared the conductivities at $50°$ and $65°$ with that at $25°$ *after* heating, in calculating the temperature coefficients. From these temperature coefficients and the original conductivities at $25°$, the true conductivities at the higher temperatures are calculated.

The apparent temperature coefficient for alcohol itself varies, as has been said, with the age and previous history of the sample; in fact the absorption of impurities by the alcohol from the vessel or by the platinum electrodes from the alcohol, together with the time change in conductivity, due, as supposed by Pfeiffer, to saturation with air, may entirely mask the true temperature effect. However, it was evident that while for ordinary alcohol with a conductivity down to about 0.3×10^{-6}, the temperature coefficient, like that for dilute solutions of salts, is high, for the purest alcohol obtained it was much smaller, if indeed it was not zero or even negative. Thus the conductivity of one sample of alcohol originally

0.3 × 10^{-6} at 25° was increased by 50 per cent when the temperature was raised to 50° C., while the conductivity of another sample rose from 0.110 at 20° to only 0.112 at 30° and gave 0.116 when again cooled to 20°; another gave sensibly the same conductivity, 0.138, at 20° and 35°. A conductivity of 0.22 at 25°, which was practically unchanged before and after heating, was reduced to 0.185 at 50°, indicating a *negative* temperature coefficient of —0.007 per degree. At 0° the conductivity was always found to be less than at 25°. A proper determination of this point, which would be of considerable interest, was outside the scope of the present investigation.

Only one substance has so far been studied with any completeness. Potassium iodide was chosen because it could be readily obtained pure (my sample gave: iodine, 76.37 and 76.44 per cent; calculated, 76.42; contained no iodate and barely perceptible traces of other halogens, and gave a clean violet flame test), and on account of the number of researches in which this substance has been included and which are available for comparison. Lithium chloride was also investigated but the figures given are subject to revision. One series of measurements was made with lithium bromide to which much weight cannot be attached as, owing to its hygroscopic character, a considerable amount of moisture was introduced with the salt.

One experimental point of some importance remains to be mentioned. Results differing by several per cent could be obtained for the resistance of the alcohols and most dilute solutions according as the connections of the telephone were made one way, or the wires interchanged. This asymmetry of the telephone, noticed by Kohlrausch, must not be neglected when working with very dilute solutions, for as its disturbing effect is not constant, the relative values for large and small resistances will not be correctly measured. As soon as discovered, the error was eliminated by taking the mean of the resistances found in the two positions, two or more readings on the bridge being taken each way. Comparison of numerous readings so obtained shows that the

proportional error increases roughly proportionately to the resistance, averaging about ±0.15 per cent for a resistance of 1000 ohms, ±1 per cent for about 7000 ohms, ±2 per cent for 15000 ohms, and so on. It should be directly determined, where appreciable, as variations from ±3 to ±7 per cent were found with alcohols giving resistances of 45,000 to 50,000 ohms. Some of the results in the earlier series have been corrected by means of these averages, the effect on the molecular conductivity found being only a small fraction of a unit.

Resistances were measured by the usual Kohlrausch method. It need hardly be mentioned that thermometers, bridge wire, weights, etc., were carefully calibrated. Molecular weights are calculated on the basis $o = 16$. The volumes are expressed in *true* liters. The standard temperature adopted for the making up of solutions was 20°, and where the solutions differed appreciably from this, they were corrected with the approximate expansion coefficient, 1.001 per 1° C. In Table I. are given only the results for high dilutions; the numerous results at dilutions below 1000 vary so little from a regular curve (about ±0.2 unit) that the individual observations have no particular interest. The figures in brackets are those which are obviously erroneous. Only the last three series were carried out with all the precautions described above, and all the results so obtained are given.

Table I.—*Molecular Conductivities in Reciprocal Ohms of Potassium Iodide at 25° at High Dilutions.*

$V \times 10^{-3}$ liters.	μ	$V \times 10^{-3}$ liters.	μ	$V \times 10^{-3}$ liters.	μ
Series I.		Series III.		Series V.	
0.98	43.8	12	48.36	2.95	47.1
24.4	48.5	149.6	[69]	8.52	48.26
179.5	[59]			51.8	46.5
				129.3	47.2
Series II.		Series IV.		Series VI.	
3.92	47.3	2.23	46.83	4.0	47.0
12.58	46.6	22.7	49.4	11.5	47.81
31.19	[51]	141.0	[43.4]	20.1	47.88
31.57	48.6	142.3	49.3	148.6	44.6
62.9	44.8	452.0	46.1	Series VII.	
157.3	[69]			10.1	49.11
				17.5	47.7

Table II.—Ratios of Molecular Conductivity of Potassium Iodide
at $t°$ to its Value at 25°.

V liters.	$t = 0°$.	18°.	50°.	65°.	78°.
12	0.673	0.904	1.335	1.5	....
13.1	0.67	....	1.39	(1.53)	1.73
16	0.67	0.90	1.34	1.55	....
32	0.672	0.90	1.36	....	....
64	0.665	0.90	1.38	1.6	(1.8)
128	0.655	0.89	1.41	....	....
250	0.64	0.89	1.44	1.63	(1.85)
500	0.64	0.889	1.47	....	....
1000	0.63	0.888	1.48	1.8	(2.1)
5000	0.63	0.885	1.486	1.8	....
10000	0.62	0.884	1.488	1.83	2.18

Table III.—Molecular Conductivities of Potassium Iodide.

V.	0°.	18°.	25°.	50°.	65°.	78°.
10	(14.8)	20.1	22.2	29.7	(34)	....
12	15.4	20.8	23.0	30.5	35.2	(40)
13.1	15.6	21.0	23.3	31	(35.8)	40.5
16	16.3	21.7	24.1	32.4	37.3	...
32	18.5	24.8	27.5	37.4	43	...
64	20.8	28.0	31.1	43.0	(50)	...
128	23.0	31.4	35.0	49.5	57	(64)
250	24.6	34.1	38.2	55	63	...
500	26.4	36.9	41.4	60.4	69	...
1000	27.9	39.1	44.0	65	75	(90)
5000	30.0	42.3	47.8	71	87	...
10000	30.1	42.8	48.4	72	88	107.2
20000	30.1	42.85	48.5	72	89	

Table IV.—Ionization of Potassium Iodide $\left(\alpha = \dfrac{\mu_v}{\mu_{max}}\right)$.

V.	0°.	18°.	25°.	50°.	65°.	78°.
10	0.49	0.47	0.458	0.41	0.38	....
12	0.51	0.485	0.475	0.42	0.40	0.37
16	0.54	0.51	0.497	0.45	0.42	....
32	0.615	0.58	0.567	0.52	0.48	....
64	0.69	0.65	0.641	0.60	0.56	....
128	0.765	0.73	0.722	0.69	0.64	(0.6)
250	0.80	0.795	0.788	0.765	0.71	....
500	0.88	0.86	0.855	0.84	0.78	....
1000	0.93	0.91	0.908	0.90	0.84	(0.85)
5000	0.997	0.99	0.986	0.99	0.98	....
10000	1.000	1.00	0.998	1.00	0.99	1.00
20000	1.000	1.00	1.000	1.00	1.00	1.00

The two extreme values at 78°, $V = 13.1$ and $V = 10000$, were the only results which I had time to determine by direct measurement in the sealed cells described above; the others are obtained by extrapolation and are naturally only rough approximations. Table IV. gives the degree of ionization calculated from the usual equation, $\alpha = \dfrac{\mu_v}{\mu_{max}}$. Compared with the values obtained by Prof. Jones,[1] by the boiling point method, the ionization found is decidedly higher, the dissociation of a decinormal solution being about 35 per cent against 25 per cent found by him, although the disagreement is much less than when the values for the conductivity are taken at lower temperatures. My own ebullioscopic determinations, as far as they have been carried, indicate approximately the same results as those of Prof. Jones.

The main interest in the above figures is in the values obtained at dilutions of over 10,000 liters. Up to 5,000 liters it is not only easy to obtain concordant results, but the values obtained, when plotted according to the Kohlrausch method against the reciprocal of the cube root of the volume, give, not a straight line as in the case of aqueous solutions of salts in the same interval of concentration, but a smooth curve slightly convex towards the dilution axis. Extrapolation from this would give a value of about $\mu_\infty = 56$ at 25° instead of 49, the highest reliable value obtained, and the values at 50,000 and 150,000 liters would be 52 and 53, respectively.

In the earlier series, before the source of error in the change of conductivity of the solvent due to the flasks cleaned in the old way was discovered, even higher (but discordant) values were obtained, from which it was thought that there might be a rapid increase in μ at very high dilutions, as has been surmised by other investigators using nonaqueous solvents. It is plain, however, that when the precautions described above are taken, the values, which agree as closely as could be expected where the correction for the conductivity of the solvent amounts to from 10 to 30 per cent of the whole, become practically constant between 20,000 and 40,000 liters and *decrease*

[1] Z. physik. Chem., **31**, 114 (1899).

at greater dilutions. This behavior is similar to that of acids and bases in aqueous solutions at about one-tenth the dilution, and may possibly be due, as is supposed in that case, to mutual interaction of the ions of solvent and solute.[1] Following the custom in the latter case, I have calculated the ionization from the *maximum* value of μ actually given by the experiments.

Thinking it possible that traces of water, such as must always be present even in the best alcohol, might produce a disproportionately great effect on the conductivity, 0.2 to 0.3 per cent by weight of conductivity water was added from a graduated 2 cc. pipette to some samples of alcohol, and to certain solutions. When due care was exercised to prevent contamination from the glass, the gain in conductivity did not exceed 0.01×10^{-6} and in some cases there was no change, or a slight decrease, from which it appears that minute traces of water cannot have any very deleterious effect. As a further test of this, three very dilute solutions were made up with the aqueous alcohol mentioned before, containing 0.8 per cent of water, and giving the very low conductivity 0.2×10^{-6}; at dilutions of 1760, 5500, and 22,000 liters the molecular conductivities 45.85, 47.5, and 44.2 were found, the first two being in close agreement with the values in absolute alcohol, the last agreeing with what would be found in the latter solvent at somewhat higher dilutions.

The results obtained with lithium chloride and bromide are given below; they are not believed to be as accurate as those with potassium iodide:[2]

Table V.—Molecular Conductivity of Lithium Chloride at 25°

Series I.		Series II.		Series III.		Series IV.	
V.	μ.	V.	μ.	V.	μ.	V.	μ.
36.1	20.6	11.37	15.1	67.3	22.5	33.9	19.8
192.0	28.5	85.5	24.2	336.5	29.6	637	31.2
6000	39.1	5345	35.9	5610	36.0	39800	37.1
24000	37.3			33650	39.1		

[1] Whetham: Z. physik. Chem., **55**, 200 (1906).

[2] The lithium chloride gave only 78.9 per cent chlorine instead of the calculated 83.4, from which it appears to have been somewhat basic. In the case of lithium bromide allowance had to be made for 24 per cent of water in salt.

Table VI.—*Ratios of Molecular Conductivity of Lithium Chloride to μ_{25}.*

V.	20°.	35°.	65°.
11.37	....	....	1.56
36.1	0.88	1.15	1.59
192.0	0.91	1.15	1.63
5345	....	....	1.88
6000	0.88	1.13	1.77

Table VII.—*Molecular Conductivity and Ionization of Lithium Chloride.*

V.	μ_{25}.	α_{25}.	μ_{65}.	α_{65}.
10	15	0.39	..	..
12	16.0	0.42	24	0.33
16	17.1	0.45	..	..
32	19.8	0.52	..	..
64	22.6	0.59	..	..
128	26	0.68	..	..
250	29	0.76	48	0.67
500	31.5	0.83	..	..
1000	33.5	0.88	..	..
5000	37	0.97	68	(0.95)
10000	37.5	0.99	..	..
20000	38	1.00	(72)	(1.00)

Table VIII.—*Molecular Conductivity and Ionization of Lithium Bromide at 25° and 65°.*

V.	μ_{25}.	μ_{65}.	$\mu_{65} \div \mu_{25}$.	α_{25}.	α_{65}.
14	18	30	1.66	0.44	0.4
54	25	43	1.70	0.61	0.57
5400	41	75	1.84	(1.00)	(1.00)

Summary of Results.

1. The precautions necessary to obtain reliable results for the conductivity of alcoholic solutions up to dilutions of 20,000 to 50,000 liters have been ascertained. A source of error in the contamination from glass vessels in which water has been dried has been pointed out.

2. The conductivity of potassium iodide has been measured up to 450,000 liters and the molecular conductivity has been shown to reach a maximum of 48.5 ± 0.5 reciprocal ohms at 25° at about 20,000 liters. A similar maximum appears to exist at all temperatures.

3. From measurements at 0°, 15°, 20°, 25°, 50°, 65°, and two measurements in sealed cells at 78°, the ionization coefficients have been calculated for all concentrations and temperatures up to the boiling point.

4. The temperature coefficients increase with rising temperature, slightly for the stronger solutions and much more noticeably for very dilute solutions. At any given temperature the temperature coefficient increases with increasing dilution.

5. The ionization decreases considerably with rising temperature. A 0.1 normal solution is dissociated 49 per cent at 0°, 46 per cent at 25°, and about 35 per cent at the boiling point.

6. The temperature coefficient for pure alcohol is much less than for alcohol with a conductivity of 0.3×10^{-6} reciprocal ohms: it may even be negative.

I desire to express here my thanks to Professor H. C. Jones for facilities granted to me and for his friendly interest in the above research.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
    Nov. 3, 1908.

———————

REVIEWS.

STEREOCHEMISTRY. By A. W. STEWART, D.Sc., Carnegie Research Fellow, and Lecturer on Stereochemistry in University College, London. Text-books of Physical Chemistry. Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S. London: Longmans, Green, and Co. 1907. pp. xx+583. Price, $2.80.

This is one of the latest volumes in the series of Text-Books of Physical Chemistry edited by Sir William Ramsay, and the student familiar with the excellent volumes by Findlay, Sydney Young, and others, will approach it with sanguine expectation. He will be disappointed. Instead of a readable and suggestive introduction to stereochemical science, a critical résumé of work done, and a stimulating formulation of problems not yet solved, he will find a collection of hurriedly written lecture notes, more or less disconnected, sometimes contradictory.

On p. 16 is given the principle, which is by no means true, that a compound cannot be active unless it contains an asymmetric carbon atom. Again, Chapter VI. (pp. 91–93) deals

with the inosites as an "exceptional" case of optical activity. Yet on p. 87 we find the necessary and sufficient condition of optical activity correctly stated in the words of Hartwall.

On pp. 21–22 one searches in vain for a critical estimate of the concept of pseudo-asymmetry. What object does it serve? What phenomena not otherwise intelligible does it correlate?

On p. 49 we read: "As a rule both optical antipodes have exactly the same chemical actions upon inactive bodies. A few statements to the contrary are to be found in the literature but it is *possible* that they may be due to errors of observation." Indeed, such observations cannot be anything else than erroneous, and the sooner the student realizes this the better.

No less than ten pages (pp. 66–76) are devoted to the configuration of the aldoses. Yet on p. 73 we read: "From the results of other investigations, which it is not necessary to discuss here, Fischer has deduced that a close relationship exists between the pentose configurations * * * * and the hexose formulae." In other words, after ten pages of hard labor the student's knowledge of Fischer's simple demonstration will still be incomplete.

The chapter on steric hindrance is comprehensive and the most likely to prove useful, although here, too, the author might be more scrutinizing in his treatment of the subject.

The rotatory power of substances is dealt with very briefly. On pp. 11–12, however, an attempt is made to give the student an elementary working knowledge of the nature of polarized light by likening it to a paper-cutter which will pass into a book if held parallel to the covers, but will refuse to pass into the book if held at its side perpendicularly to covers and leaves. The student who needs such illustrations at all will conclude that polarized light must refuse to pass through a tourmaline plate in all directions but one. If the book is addressed to beginners, a much longer (and better) explanation should have been given. If the reader is assumed to be mature, he will either need no explanation at all, or else know how to find one in a text-book of physics.

While Stewart's book, or at least this first edition of it, cannot be welcomed with enthusiasm, one must bear in mind that much in stereochemical science is in a nascent state, and that the task of writing a good treatise on the subject is a difficult one. The investigator ought to place the new book on his shelves beside Werner's well known *Lehrbuch,* on the principle that if one single suggestion can be gleaned from the pages of a book it is worth having. M. A. Rosanoff.

PHOTOCHEMIE UND BESCHREIBUNG DER PHOTOGRAPHISCHEN CHEMIK-
ALIEN. Von H. W. VOGEL. Fünfte, völlig umgearbeitete Auflage,
besorgt von DR. ERNST KÖNIG. Berlin: Gustav Schmidt. 1907. pp.
XII + 376. Price, 11 M.

This volume forms Part I. of the "Handbuch der Photo-
graphie" and is devoted for the most part to the action of
light upon the elements, organic and inorganic compounds,
life processes of plants and animals, etc., regardless of their
connection with photography. The first chapter treats of
photo-crystallization, phosphorescence, Warnerhe's photometer,
the action of light on selenium, Bell's photophone, Korn's
system for telegraphing photographs, Sommerville's imagined
production of magnetism by light, which is recorded as a fact,
although it was repeatedly disproved twenty years ago, photo-
electricity, Crooke's radiometer, and the action of X-rays and
the radiations from radium.

The second chapter is devoted to the chemical action of
light upon the elements and their compounds, and takes up
decompositions, syntheses, and polymerizations which result
from the action of light. Later on we find a very complete
treatment of the behavior of the chemicals commonly used
in photographic processes, and the behavior of the various
light-sensitive compounds of the metals, including, of course,
the action of dyes in rendering plates sensitive to definite
regions of the spectrum.

The book forms a useful compendium, though a number of
remarkable phenomena, such as the Clayden effect, receive no
mention.   R. W. W.

METHODS AND DEVICES FOR BACTERIAL TREATMENT OF SEWAGE. BY
WILLIAM MAYO VENABLE. New York: John Wiley and Sons. 1908.
pp. VI + 236. Price, $3.00.

This little volume by W. M. Venable, concerning the bacterial
treatment of sewage, is an important addition to our list of
text-books dealing with this subject and contains a full exposi-
tion of the essential principles underlying this process. The
ideas are presented in a clear systematic manner, appealing
especially to those with limited time at their disposal, and there
is a happy combination of practical and scientific knowledge
rarely seen in books of this character. The various means by
which crude sewage may be purified are taken up in consider-
able detail, Chapter 3, for instance, considering the aerobic
and Chapter 4 the anaerobic treatment of this material,
other chapters dealing with such important subjects as the
intermittent contact system, automatic discharging devices,
and percolating filters. Two sections of the book are especially

to be commended—the one giving *seriatim* the various engineering principles involved in all systems of filtration, the other a detailed account of two actual installations, those at Fort DesMoines, Iowa, and Fort Leavenworth, Kansas, where the author was employed by the United States Government to oversee the construction of important sewage purification works. Mr. Venable's experience in these undertakings is extensively detailed, and in consequence this book becomes of great value to the practical engineer. W. W. FORD.

REFRIGERATION. BY J. WEMYSS ANDERSON. New York: Longmans, Green, and Co. 1908. pp. 242. Price, $2.25.

In his introduction the author states that this work is intended to be an elementary treatise. With this in mind he has devoted the first six chapters to a general discussion of the effects produced by heat and to the thermodynamics of gases and of such vapors as are used in refrigeration. This is followed by a full description of the various types of refrigerating machines.

The subject of "Ice Making" and "Ice Making Plants" is treated at considerable length and many illustrations showing the interior of English ice plants are given. About twenty pages are devoted to the subject of cold storage and to the insulation of cold storage rooms.

Under "Marine Refrigeration" the most recent installations of refrigerating apparatus in such steamships as the Lusitania, Mauritania, Carmania, Tropic, and Cufic are described in detail and drawings of some of the outfits are given.

The book is written in such a way that it may be understood by one not technically educated. It contains much information that is valuable and will be found to be a good elementary text-book on Refrigeration. EDW. F. MILLER.

ELEVENTH ANNUAL CONVENTION OF THE ASSOCIATION OF STATE AND NATIONAL FOOD AND DAIRY DEPARTMENTS. Held at Jamestown Tercentennial Exposition, July 16–19, 1907. New York and London: John Wiley and Sons. 1908. pp. 416. Price, $3.00 net.

The reports of the meetings of this Association are always of interest as they bring together manufacturers of foods and officials charged with the inspection of foods. The questions are discussed both from the standpoint of the inspector and the manufacturer. A review of the proceedings is difficult because of the length of the program and the large number of questions treated. Among the interesting questions discussed may be mentioned: Publicity in the Enforcement of Pure-Food Laws, by Edward K. Slater, State Dairy and Food

Commissioner of Minnestoa; Coöperation between the State and Federal Authorities, by A. H. Jones, State Food Commissioner of Illinois; The Element of Uniformity in National and State Food Laws, by H. Q. Emery, State Dairy and Food Commissioner of Wisconsin; Diabetic Foods, by A. L. Winton, of the Chicago branch laboratory of the United States Department of Agriculture; "Like Substances," by James H. Shepard, State Analyst, South Dakota; Bleaching of Flour, by E. F. Ladd, State Commissioner of North Dakota.

Several addresses of special value to the dairy interests were given and difficulties experienced in the several States and by manufacturers in meeting the requirements of the laws of the various States were discussed.   W. D. BIGELOW.

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ERRATA.

Vol. 40, p. 294, l. 4, formula should read $\dfrac{(CH_3)_2C.OH.CO.NH}{(CH_3)_2C.OH.CO.NH}>CO$

Vol. 40, p. 414, l. 7, after Düsseldorf, insert Leipzig: Verlag von Wilhelm Engelmann.

I

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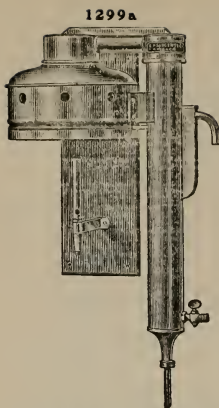
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